Soft matter crystallography—complex, diverse, and new crystal structures in condensed materials on the mesoscale

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An increasing variety of crystal structures has been observed in soft condensed matter over the past two decades, surpassing most expectations for the diversity of arrangements accessible through classical driving forces. Here, we survey the structural breadth of mesoscopic crystals—formed by micellar systems, nanoparticles, colloids etc.—that have been observed both in soft matter experiments and coarse-grained self-assembly simulations. We review structure types that were found to mimic crystals on the atomic scale, as well as those that do not correspond to known geometries and seem to only occur on the mesoscale. While the number of crystal structure types observed in soft condensed matter still lags behind what is known from hard condensed matter, we hypothesize that the high tunability and diversity of building blocks that can be created on the nano- and microscale will render a structural variety that far exceeds that of atomic compounds, which are inevitably restricted by the “limitations” imposed by the periodic table of elements and by the properties of the chemical bond. An infusion of expertise in structural analysis from the field of crystallography into the soft condensed matter community will establish the common language necessary to report, compare, and organize the rapidly accruing structural knowledge gathered from simulations and experiments. The prospect of new materials created in soft matter and new, length-scale-spanning insights into the formation of ordered structures in both hard and soft condensed matter promise exciting new developments in the area of self-assembled mesoscale materials.

INTRODUCTION

It has been argued that complex building blocks beget complex assemblies—that the creation of complex materials can only be achieved through intricate and highly specific interactions. Increasingly, however, complex structures have been shown to arise on the mesoscale from deceptively simple particle systems. In experimental studies, a growing number of various crystal structures can be formed from nanoparticles, micellar systems, and colloids, whereas most computational studies on the mesoscale use isotropic pair potential, anisotropic faceted polyhedral shapes, or patchy particle models (see Fig. 1).

Many of the structures formed in experiments and simulations of particulate matter on the mesoscale are being found to form in particulate matter on the mesoscale and are geometrically equivalent to crystals on the atomic length scale. While highly complex crystal structures on the atomic scale—e.g., quasicrystals and complex intermetallics—are stabilized by electronic interaction and forces at the quantum level, mesoscale crystal structures are formed due to classical interactions. The observation of various intricate crystal structures self-assembling from simple numerical simulations—operating only through classical thermodynamics—is therefore a logical extension of the experimental detection of such structures in soft condensed matter.

Another factor sets soft matter apart from hard matter: the highly discrete choice of building blocks on the atomic scale—dictated by the periodic table—is in stark contrast to the dizzying number of parameters at the disposal of soft materials scientists and engineers. The enormous tunability of building blocks on the mesoscale implies that there is no reason to restrict ourselves to targeting structures known from compounds on the atomic scale when creating new ordered mesoscale materials.

In order to access the full diversity of feasible crystal structure types as design targets in soft condensed matter, we must know which structures are technically possible. Currently, all those that we know of and can easily search for through existing databases—such as the Inorganic Crystal Structure Database (ICSD) and Pearson’s Crystal Data—are atomic or molecular struc-

FIG. 1. Top: Types of mesoscale particles: nanoparticles or nanodots, micelles, colloids. Bottom: Types of computational models most commonly used to simulate mesoscale systems: isotropic pair potentials, faceted (often: hard) polyhedra, anisotropic patchy particles.

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structures, whose geometries are dictated by the properties of the chemical bond. If we aim to design completely novel structures, we must invent new ways of looking for them, while adhering to the tried and tested methods from the crystallographic playbook to describe and analyze said structures.

BACKGROUND: STRUCTURAL COMPLEXITY AND VARIETY

Within the traditional realm of crystallography, where all ordered structures can be represented with 230 space groups and captured in a parallelepiped that serves as an immutable repeat unit, the size of that unit cell can reasonably be used to measure the complexity of the crystal structure that it describes. Here, this is expressed in a notation for different crystal structure types that consists of the Pearson symbol, which specifies a structure’s Bravais lattice and the number of atoms per unit cell (e.g., cF4 for the face-centered cubic close-packing of spheres, which contains 4 atoms per unit cell), as well as a prototypical compound that exhibits the respective crystal structure type (e.g., cF4-Cu in the case of the cubic-close sphere packing; more details on the crystallographic notation used here are indicated in the Appendix). Additional variations of structural complexity measures include using only the primitive unit cell’s content, as opposed to the often centered unit cells used as standard settings, or using the contents of only the asymmetric unit, i.e., the number of Wyckoff positions, which are then multiplied by rotations, rotoinversions, glide planes, and screw axes to populate the unit cell. Alternatively, the complexity of crystal structures can be expressed via a topological approach based on information theory.

While all periodic crystals can be characterized with space groups and their unit cell size therefore measured accordingly, not all crystals are periodic. Aperiodic crystals—such as quasicrystals or incommensurately modulated crystal structures—can only be described by periodic units that possess additional dimensions compared with the spatial dimensions of the crystal itself, making it impossible to compare their unit cell contents to those of classic, three-dimensional ones.

An additional degree of complexity in crystalline structures is that of intrinsic disorder. While “crystals” are inherently mostly ordered structures, disorder can still prevail within them either in statistical or correlated manners. In some cases this is the result of incomplete crystallization, but correlated or partial disorder can also be an inherent feature of a crystal structure and—while difficult to decipher—it can even present a tunable design parameter.

Some of these dimensions of structural complexity are difficult to enumerate: aperiodic crystal structures and those with correlated disorder defy the standard means of reporting crystal structures and are therefore not easily encompassed and represented in databases. Despite these gaps regarding extreme structural complexity, however, the sheer variety of crystal structures known from compounds on the atomic scale is dizzying: the ICSD, for example, contains over 200,000 entries, a majority of which can be assigned to over 9,000 crystallographically distinct structure types. It is important to keep in mind that these structure types belong to different materials classes, some of which are likely better design targets for mesoscale systems than others, e.g., the over 2,000 structure types in which intermetallic compounds have been found to occur.

REVIEW: COMPLEX CRYSTAL STRUCTURES IN HARD CONDENSED MATTER

Highly complex structures on the atomic scale have been known for over half a century: Samson described a variety of intermetallic compounds that exhibit unit cells containing over a thousand atoms and the largest known unit cell in intermetallic systems was found to contain more than 20,000 atoms. While uncommon, complex intermetals have been observed in a large variety of systems—containing different chemical elements, featuring different types of chemical bonding, and hugely varying stoichiometries—and they make up around 2% of intermetallic compounds generally. Binary and ternary intermetallics also constitute the systems where quasicrystalline structures were first discovered and later found to be all but ubiquitous. Another system discovered to exhibit quasicrystallinity on the atomic scale is a two-dimensional oxide in the Ba–Ti–O system (deposited on Pt(111) substrates).

Given the structural simplicity of most pure metals, which tend to adopt sphere packing-type structures, intermetallic systems might be the most unsuspecting and therefore most surprising candidates for producing highly complicated crystal structures. However, compounds of extreme complexity are well-known in other systems, too; oxides in particular provide a rich landscape of structural variety. One class of structures, for example, consists of intergrowths of multiple structural elements at a variety of compositions; such related but distinct structure types can be understood as a homologous series and comprise theoretically infinitely many individual compounds, e.g., Ruddlesden-Popper phases. Another category of oxides with complex structures are framework compounds: zeolites, for example, are minerals that occur in a huge variety of crystal structures—with even more hypothetical frameworks—and new structures are continually being discovered. Other compounds with complex structures are, for example, clathrates, in which large cations—atomic or molecular in nature—occupy the even larger cages in a host structure. The host structures are typically formed by covalently-bonded elements such as silicon—in intermetallic clathrates—or by water molecules in clathrate hydrates. In the realm between organic and inorganic crystal structures,
lie more categories of framework compounds: metal-organic frameworks (MOFs)\textsuperscript{39} and more recently discovered covalent-organic frameworks (COFs)\textsuperscript{10} which also represent a dizzying variety of structure types and tunable geometrical and chemical properties. In a nutshell: complexity is present in crystal structures on the atomic scale in a multitude of ways independent of the building blocks’ complexity.

**REVIEW: COMPLEX CRYSTAL STRUCTURES IN SOFT CONDENSED MATTER**

Similarly to metals, soft matter systems were initially thought to mainly form simple structures. While the self-assembly of colloidal spheres into sphere packings was observed early and widely\textsuperscript{11–13} and the same structure types have been observed in a growing variety of systems, such as functionalized nanoparticles (cF4-Cu, cI2-W, hP2-Mg)\textsuperscript{45–46}—an increasing diversity of structures has been uncovered over the past 15 years (see Tab. 1 and Fig. 2) through varying particle attributes such as explicit interaction potential and anisotropic particle shape. In addition to these attributes, however, there are other parameters that open up a high-dimensional design space and Fig. 2) through varying particle attributes such as explicit interaction potential and anisotropic particle shape. In addition to these attributes, however, there are other parameters that open up a high-dimensional design space

Other structure types that are ubiquitous in intermetallic compounds are closely related to topologically close-packed phases: γ-brass cI52-Cu2Zn\textsubscript{8} has been observed in simulations of hard truncated dodecahedra\textsuperscript{22} and repulsive clusters of dodecahedral spheres\textsuperscript{50} in other hard shapes\textsuperscript{81} as well as isotropic pair potentials\textsuperscript{70} and β-manganese cP20-Mn has been observed in simulations of pentagonal dodecahedra, as well as some of its augmented versions\textsuperscript{59} and corresponding repulsive sphere clusters\textsuperscript{50} and also isotropic pair potentials\textsuperscript{47}. A sphere packing with a more disparate size ratio—and therefore 12- and 13-, as well as a 24-coordinated site—is cF112-NaZn\textsubscript{13}, which has been observed both in binary systems of nanoparticles\textsuperscript{47} and in simulations of polydisperse systems\textsuperscript{29}. In similar binary systems of nanoparticles, the hP6-CaCu\textsubscript{5} structure type has been observed, exhibiting 12- and 18-coordinated sites\textsuperscript{27}.

Larger discrepancies in particle size in multi-component systems can stabilize structures such as hP3-AlB\textsubscript{2}, which has been observed in binary systems of nanoparticles\textsuperscript{29} as well as DNA-functionalized colloids\textsuperscript{70} and hP6-AlMgB\textsubscript{4}—a ternary superstructure of hP3-AlB\textsubscript{2}—observed in a ternary system of nanocrystals\textsuperscript{100}, cP7-CaB\textsubscript{6}, also observed in binary nanoparticle systems\textsuperscript{101}. Another binary structure type stabilized in this manner is the salt-type cP2-CsCl, which was also observed in DNA-functionalized nanoparticles and colloids\textsuperscript{102} and in binary systems of hard spheres with attractive interactions between unlike particles\textsuperscript{103}.

The above-mentioned systems modify shape parameters of the constituent particles, in particular via anisotropy in systems of faceted polyhedra or compound shapes such as rigid bodies of multiple spheres, or also via the size ratio in multi-component systems. An even larger variety of crystal structures becomes accessible if specific interaction patterns can be implemented, which can drive the assembly of multi-component
FIG. 2. Known crystal structure types that were found in experimental and computational studies on the mesoscale. Particle positions are colored according to their coordination numbers (with gray particles indicating Wyckoff positions with identical coordination numbers occupied with distinct particle types): maroon = 0–2, red = 4, orange = 5–6, yellow = 8, green = 9–11, cyan = 12, blue = 13–15, purple = 16–24. Images are generated using CrystalMaker®.

phases via multivalent functionalizations. Examples of the new types of structures that can be attained in this manner are: another salt-type structure formed by nanoparticles—cF8-NaCl (also observed in binary systems of nanoparticles) and a Zintl-phase—cF16-NaTl (or B32, also called “double-diamond”; also observed in surfactant micelles). Both with nanocrystals with polymer-mediated interaction and with DNA-functionalized nanoparticles with multivalent interactions but identical cores, the simple cubic structure cP1-Po could also be assembled; the same structure type was also observed in binary systems of hard spheres with attractive interactions between unlike particles, in systems of cubic colloids, and in simulations of hard polyhedra.

More recently, tetrahedrally-shaped colloidal clusters have been found to assemble this structure on the mesoscale, whereas simulations have discovered diamond-type crystals in systems of patchy particles, as well as in systems of hard truncated tetrahedra and isotropic pair potentials. The binary variant of the diamond structure type, cF8-ZnS, was found in binary systems of hard spheres with attractive interactions between unlike particles.

Another family of crystal structure types with coordination number 4 are clathrates (which on the atomic
TABLE I. Known crystal structure types that were found in experimental studies on the mesoscale, and in related coarse-grained simulation studies. The experimental mesoscale systems include: colloids (e.g., spherical shape (spheres), binary systems (2)), nanoparticles (NP; e.g., one-component (1), binary (2), ternary (3); multivalent (MV) systems; binary DNA-functionalized nanoparticles (2-DNA)), micelle-forming systems (e.g., block copolymers (BCP), dendrimers (dendr.), surfactants (surf.)); as well as shape amphiphiles (SA). The model systems used in simulations include isotropic particles (iso.; i.e., hard spheres (HS) or polydisperse sphere systems (PS)), functionalized hard spheres (fHS), or point particles interacting via Lennard Jones (LJ) or other isotropic pair potentials (IPP)) and anisotropic particles (ani.; e.g., anisotropic polyhedra (AP; as well as corresponding binary systems: 2-AP), sphere clusters (SC), combinations of spherical clusters and spheres (SC+S), or patchy particles (PP)).

| Structure type | Pearson symbol | Space group | Colloidal system | Experimental Studies | Simulation Studies |
|----------------|---------------|-------------|------------------|---------------------|-------------------|
| Sphere packings |               |             |                  |                     |                   |
| cF4-Cu         | Fm3m          | ccp / "fcc" | A1               | colloids            | L1, HS, IPP, AP, SC |
| cI2-W          | Im3m          | "bcc" / A2  |                  | colloids            | L1, HS, IPP, AP, SC |
| hP2-Mg         | P63/mmc       | hcp / A3    |                  | colloids            | L1, HS, IPP, AP, SC |
| tP2-CuAu       | P4/mmm        | L1          |                  | colloids            | L1, HS, IPP, AP, SC |
| cP4-Cu3Au      | Pm3m          | L1          |                  | colloids            | L1, HS, IPP, AP, SC |
| tI2-Pa         | I4/mmm        | A1          |                  | colloids            | L1, HS, IPP, AP, SC |
| Frank-Kasper phases |               |             |                  |                     |                   |
| cF24-MgCu2     | Pd3m          | C15 (Laves) |                  | colloids            | L1, HS, IPP, AP, SC |
| hP12-MgZn2     | P63/mmc       | C14 (Laves) |                  | colloids            | L1, HS, IPP, AP, SC |
| hP24-MgNi2     | P63/mmc       | C36 (Laves) |                  | colloids            | L1, HS, IPP, AP, SC |
| cP8-Cr3Si      | Pm3n          | A15         |                  | colloids            | L1, HS, IPP, AP, SC |
| tP30-CrFe      | P4/mmm        | σ-phase / D8 |                  | colloids            | L1, HS, IPP, AP, SC |
| hP7-Zn4Al3     | P6/mmm        | Z-phase     |                  | colloids            | L1, HS, IPP, AP, SC |
| dodecahedral quasicrystals (12-QC) |               |             |                  | colloids            | L1, HS, IPP, AP, SC |
| More intermetallic structures types |               |             |                  |                     |                   |
| cF52-Cu3Zn8    | I43m          | γ-brass / D8 |                  | colloids            | L1, HS, IPP, AP, SC |
| cP20-Mn        | P432          | β-Mn / A13  |                  | colloids            | L1, HS, IPP, AP, SC |
| cF112-NaZn13   | Fm3c          | D23         |                  | colloids            | L1, HS, IPP, AP, SC |
| hP6-CaCu5      | P6/mmm        | D2d         |                  | colloids            | L1, HS, IPP, AP, SC |
| hP3-AlB2       | P6/mmm        | C32         |                  | colloids            | L1, HS, IPP, AP, SC |
| hP6-AlMgB4     | P6/mmm        | C12         |                  | colloids            | L1, HS, IPP, AP, SC |
| cP7-CaB6       | Pm3n          | D21         |                  | colloids            | L1, HS, IPP, AP, SC |
| Significant ionic contributions (salts, Zintl phases, etc.) |               |             |                  |                     |                   |
| cF8-NaCl       | Fm3m          | rocksalt / B1 |                  | colloids            | L1, HS, IPP, AP, SC |
| cP2-CoCl       | Pm3n          | B2          |                  | colloids            | L1, HS, IPP, AP, SC |
| cF16-NaTi      | Fd3m          | B32         |                  | colloids            | L1, HS, IPP, AP, SC |
| cF8-ZnS        | F4m           | zinchende / B4 |                  | colloids            | L1, HS, IPP, AP, SC |
| cF12-CaF2      | Fm3m          | fluorite / C1 |                  | colloids            | L1, HS, IPP, AP, SC |
| cP4-ReO4       | P23           | D09         |                  | colloids            | L1, HS, IPP, AP, SC |
| hP12-SiO2      | P63/mmc       | β-tridymite / C10 |                  | colloids            | L1, HS, IPP, AP, SC |

Low coordination numbers:

| Structure type | Pearson symbol | Space group | Colloidal system | Experimental Studies | Simulation Studies |
|----------------|---------------|-------------|------------------|---------------------|-------------------|
| cP1-Po         | Pm3m          | A6          |                  | colloids            | L1, HS, IPP, AP, SC |
| tI4-Sn         | I41/amd       | β-tin / A5  |                  | colloids            | L1, HS, IPP, AP, SC |
| cP16-Li        | Fd3d          | G4           |                  | colloids            | L1, HS, IPP, AP, SC |
| cI2-Si         | Ia3           |              |                  | colloids            | L1, HS, IPP, AP, SC |
| tI2-CdHg       | I4/mmm        |              |                  | colloids            | L1, HS, IPP, AP, SC |
| hP1-Ca0.15Sn0.85 | P6/mmm     |              |                  | colloids            | L1, HS, IPP, AP, SC |
| cP4-Li         | P432          |              |                  | colloids            | L1, HS, IPP, AP, SC |
| cF8-C          | Fd3m          | diamond / A4 |                  | colloids            | L1, HS, IPP, AP, SC |
| cP54-K3Si23    | Pm3n          | clathrate-I |                  | colloids            | L1, HS, IPP, AP, SC |
| cI432-Te7+Si20−x | Fd3c         |              |                  | colloids            | L1, HS, IPP, AP, SC |

whereas in hard polyhedral particles the highly complex clathrate-type crystal structure cI432-Te7+Si20−x has been observed. In binary systems of nanoparticles, the cP5-Fe4C structure type was observed, consisting of tetrahedral Fe4C colloidal “molecules.”
It should be noted that lower-coordinated structures are strictly-speaking possible, such as 3-connected networks (e.g., the gyroid or double-gyroid structures) 2-connected columnar structures, or 1- or 2-connected quasi-molecular structure types. In polymeric systems, the gyroid structure is observed as one of infinitely extended domains with minimal surface area rather than one of 3-connected particles, which is why we chose not to include it in this overview. Additionally, it seems to be quite rare to see such low-coordinated structures that correspond to known structures—in particular in experimental studies of soft condensed materials—although a few without atomic equivalents are mentioned below to have occurred in simulation studies.

Different degrees and types of order form in soft-condensed-matter systems: in addition to traditional, periodic crystal structures (see Tab. 1), e.g., aperiodic quasicrystals 5111 degenerate crystals,112 mesophases such as liquid and plastic crystals,19 are observed.

ORIGINS OF STRUCTURAL COMPLEXITY ON THE MESOSCALE

Many of the complex structures that arise on the mesoscale are due to the interplay of multiple, competing interactions that complicate crystal structure formation, such as local vs. global packing in anisotropic particles,113 and soft corona vs. hard core interactions in isotropic particles.114

Between particles with anisotropic shapes, implicit directional entropic forces emerge that govern the formation of ordered structures.102,111,115 When different local motifs compete with one another, crystallization can be suppressed117 and similarly to hard condensed matter, phase transitions between different crystal structures can be induced via thermodynamic parameters such as pressure or via particle properties such as shape.115,120 Transition between the disordered and ordered states during the self-assembly process of particles with anisotropic shapes are often preceded by the emergence of distinct local motifs121 and can feature different behaviors, such as nucleation and growth,122,123 the formation of disordered precursor phases,111 the formation of precursor mesophases,124,125 or the gradual emergence of ordered domains.115,125

Most mesoscopic interactions are largely isotropic, but due to the inherent sphericity of the particles themselves (micelles or non-patchy colloids) or due to the “shielding” of anisotropic features such as shape due to a corona with which, for example, nanoparticles are often functionalized in order to enable their self-assembly into ordered structures (e.g., with DNA or polymers). For diblock copolymers, the formation of Frank-Kasper structures—with unequal domain volumes—instead of simple sphere packings seems to result from the relative stiffness of the corona, leading to the formation of aspherical domains.126 Early work discussed how star polymers and polymer coils can be described as soft colloidal particles.127 Inorganic nanoparticles that are functionalized with polymer brushes, for example, are said to interact via effective potentials that exhibit features of competing interactions—of hard, repulsive core interactions and soft, attractive interactions of the particle coronas.114,115,116 While some studies have explicitly described experimental systems of soft matter particles with isotropic pair potentials,117,118 effective potentials between mesoscopic particles are often simply assumed to correspond to certain isotropic pair potentials, and establishing a direct connection between specific particle systems and pair interactions that mimic their physical behavior remains a challenge.20,119,120 The radial complexity of isotropic pair potentials can be viewed as an approximation of the complexity of potentials of mean force in many-body systems,13 and isotropic pair potentials have been found to achieve agreement between coarse-grained self-assembly simulations and soft-matter experiments.114,115

REVIEW: DISCOVERY OF NEW CRYSTAL STRUCTURES ON THE MESOSCALE

While the increasing structural diversity that has been realized both experimentally and in simulations is exciting, the discovery of completely new crystal structures on the mesoscale that have no atomic equivalents opens up an even larger realm of structural possibility. Our recent study of a large variety of isotropic pair interactions revealed the self-assembly of particles into previously unknown structure types across a wide range of complexities (from hP1 to cI100), symmetries (cubic, tetragonal, hexagonal, and orthorhombic), and effective “chemical bonding states”, expressed via their coordination numbers from 4 to more than 12.126 Similar interaction potentials had previously been found to assemble a one-component icosahedral quasicrystal, which is structurally completely distinct from known metallic quasicrystal structures: the observed structure exhibits local particle environments with 4–7 nearest neighbors, as opposed to metallic quasicrystals, which have high coordination numbers of 12 to 14, characteristic of sphere-packing-like geometries.61 In high-pressure simulations of a different series of isotropic pair potentials, other quasicrystals with mostly low coordination numbers were found. These quasicrystals exhibit octagonal, decagonal, and dodecagonal (i.e., 8-fold, 10-fold, and 12-fold) symmetries and also do not correspond to known crystal structures.111

In binary systems of octahedral colloidal clusters and spherical colloids, a new cP6_3A2B1 structure type (space group P43m) was observed.128 In simulations of polydisperse particles, a complex Frank-Kasper phase oS276, which is also a decagonal quasicrystal approximant, was observed.129 In systems of hard polyhedra, more structures without atomic equivalents were found: a do-
decagonal quasicrystal made up of tetrahedra\(^5\) a “β-tin”-like structure that constitutes a diamond-derivative structure \(tI4\)-\(X\)\(^{115}\) etc.\(^{110}\)

In studying the self-assembly behavior of particles that interact via an isotropic pair potential with a \(cF8\)-\(C\)-forming (i.e., diamond-type) ground state\(^{112}\) a variety of crystal structures were discovered that span both common densely packed structures, as well as crystals with low coordination numbers between 2 and 8\(^{54}\). Some of these low-coordinated structures seem to correspond to those discovered by other computational studies (\(hP2\)-\(X\), \(tI4\)-\(X\), etc.), while several are likely unique observations.

It has been shown via free-energy calculations that isotropic particles of two different sizes can stabilize a variety of structures if they are mixed, both with simple repulsive square-shoulder pair potentials\(^1\)\(^{13}\)\(^{16}\) as well as simple attractive interaction potentials\(^2\)\(^{13}\)\(^{16}\). However, it should be noted that such ground-state calculations—similar to studies that investigate dense packings of different types of particles—do not necessarily reveal structures that are kinetically achievable via assembly and will therefore not be discussed further here.

As in simulations, a number of novel crystal structures have been discovered in experimental studies on the mesoscale in recent years. In some cases, the exact determination of their structure is challenging—by definition—due to the lack of points of comparison, paired with the sometimes limited structural information obtainable due to suboptimal crystallinity or limited sample sizes. Additionally, previously unknown structures are described in the literature in a variety of ways, which complicates matching them against reference data. In some cases, structures are reported directly via their unit cells, as for example in the case of two new crystal structures found in a binary system of spherical and tetrahedral colloidal particles: a \(cF36\)-\(AB8\) phase (space group \(Fm3m\)) and a \(P10-\text{AB1}\) phase (space group \(P4m2\)) both not equivalent to any known crystal structure types on the atomic scale. In a binary system of nanocrystals, an \(hP34-\text{AB25}\) structure (space group \(P6m2\)) was observed\(^{118}\). Also in binary nanoparticle systems, the structure type \(cP14-\text{AB13} \ (Pm3m)\) was reported\(^{17}\)\(^{119}\).

Some structures are described by proxy through related structure types, as has been done in the case of \(cI14-\text{A2B12} \ (\text{space group } Im3m)\). This structure type was observed in binary systems of (DNA-functionalized) nanoparticles, as well as colloids\(^{657}\)\(^{68}\)\(^{16}\) and its structure was reported as being equivalent to \(cI132-\text{Cs8C60}\), where one type of particle (A) takes on the positions of C\(_{60}\) molecules in the unit cell. Although it has a relationship to a molecular structure type, the exact \(cI14\) version had never been observed on the atomic scale—presumably due to the extreme size ratio between A- and B-type particles necessary to stabilize this arrangement.

Another example of a structure description by proxy is the \(cP54-K_{3}\text{Si}3\) (or “clathrate F”) derived structure found in DNA-functionalized nanoparticles shaped like trigonal bipyramids\(^{159}\) here, each atomic position in the basic structure is actually occupied by a tetramer of trigonal bipyramids, with the nanoparticles effectively occupying the edges or bonds between the original atomic positions. Each atomic position in the Si-framework is connected to 4 other positions (with each bond being shared between 2 positions), leading to a particle count of \(46 \times 4 / 2 = 92\) trigonal bipyramids per unit cell. The resulting \(cP92\)-\(X\) structure type\(^{101}\) (space group \(Fm\text{3}n\)) has no equivalent on the atomic scale.

Finally, deformable triblock Janus colloids self-assembled open structures, which were described via their relationships to crystal structures with ionic bonding character: a scaffold of vertex-sharing tetrahedra, sometimes termed the “pyrochlore” structure, which consists of only the Cu-sites in the \(cF24\)-\(MgCu2\) Laves phase structure type or only the O-sites in the \(cF24\)-\(SiO2\) cristobalite structure type\(^{159}\) the same structure was also observed in simulations of particles interacting via a repulsive square-shoulder pair potential\(^{152}\). Triblock Janus colloids also formed a scaffold of vertex-sharing octahedra, which consists of only the O-sites of the \(cP5\)-\(CaTiO3\) perovskite structure type\(^{154}\).

NEW PROPERTIES ON THE MESOSCALE?

Materials for a wide range of optical or photonic applications have been created from a variety of soft matter systems—block copolymers, colloids, nanoparticles, and biological materials\(^{153}\). Self-assembled materials with photonic band gaps have been subject to in-depth investigations for many years, promising applications as elements of optical circuits, for improved light-harvesting, etc. Due to the known wide and robust bandgap of the diamond structure, systems that could form this structure type have been studied intensively\(^{55}\)\(^{54}\)\(^{16}\)\(^{118}\) with only very recent experimental success\(^{29}\). Complete photonic bandgaps were shown to exist in monoclinic crystal structures formed by dimer-shaped colloids\(^{153}\)\(^{156}\) as well as several layered structures on square lattices and Archimedean \(3\text{^2}.4.3.4\) tilings (to which the \(tP30\)-\(CrFe\) structure type can be mapped)\(^{157}\)\(^{159}\).

Other ordered mesostructures were found to exhibit uncommonly high refractive indices and are predicted to enable cloaking capability\(^{159}\). Crystalline mesostructures of spherical particles have potential for light-trapping applications\(^{161}\). Mixed systems of colloids with distinct glass transition temperatures can be made into optical sensors based on time-dependent film formation properties\(^{162}\).

The phononic bandstructures of mesostructures are governed by the shape of their building blocks, as well as their assembled crystal structures\(^{163}\), and the combination of particles with different sizes can increase their phononic bandgaps significantly\(^{164}\).

Colloidal semiconductor nanocrystals were found to exhibit strong interactions via their organic ligands, lead-
ing to a pathway toward exploiting coherent phonons for light sources with high-frequency modulation\textsuperscript{166}. Preferential alignment of nanoparticles along directions that have superior transport properties is necessary to create nanocrystal-derived thermoelectrics\textsuperscript{166}, and it can be achieved by an assembly process that is directed via external fields or by targeting anisotropic assembly structures\textsuperscript{167}. If nanocrystals are assembled into epitaxially connected thin films, the resulting superior carrier transport properties can pave the way toward engineering new devices such as field-effect transistors\textsuperscript{168}.

By integrating colloidal nanocrystals with metallic, semiconducting, and insulating properties, high-performance devices such as field-effect transistors can be constructed that could be the basis for developing flexible, low-cost electronics\textsuperscript{169,170}. Potential device applications of nanocrystal mesostructures also include light-emitting diodes, photodetectors, solar cell components, and memory elements\textsuperscript{171}.

Future applications of nanocrystal assemblies will also explore their quantum optical properties, such as single-photon emission, optical and spin coherence, and spin-photon interfaces\textsuperscript{172}. Via nanotransfer printing, photonic and electronic devices can therefore be manufactured in a high-throughput manner, on flexible and curved surfaces, therefore creating opportunities for large-area metamaterial fabrication\textsuperscript{173,174}. Patterning methods also allow for the fabrication of metamaterials that can be tuned in structure and function through a thermal trigger, eliciting a chiroptical response that will allow for the development of ultrathin lenses and polarizers\textsuperscript{175}.

**SEARCH AND DESIGN FOR NEW CRYSTAL STRUCTURES**

A wide variety of approaches has been applied to explore the capacity of mesoscale building blocks to form different structures. While some studies target disordered structures\textsuperscript{175} or mesophases\textsuperscript{176,177}, here we focus on the design of crystalline structures in particular.

One important consideration in the context of targeting new structures is that an otherwise powerful approach—that of inverse design—is not the most promising path forward. Inverse design has been successful at targeting crystal structures that are known from the atomic scale in a variety of mesoscale systems\textsuperscript{178} such as patchy particles\textsuperscript{179,180}, faceted anisotropic shapes\textsuperscript{181,182}, and isotropic pair potentials\textsuperscript{183,184}. However, since this pathway is based on previous knowledge of the targeted geometries, it explores only crystal structures that have been observed on the atomic scale and therefore are stabilized by highly discrete chemical elements and interactions. The vastly larger design space of structural building blocks on the mesoscale\textsuperscript{178} enables us to strive for considerably more variety among structures and motifs, which means that our exploration of the structures that can be assembled in different kinds of systems can be equally broad.

Over recent years, our ability to conduct increasingly extensive computational screenings for new structures has increased exponentially, with studies investigating for example the assembly behavior of hard polyhedra starting at discrete shapes\textsuperscript{185} and escalating to one- and two-dimensional parameter spaces in a matter of years\textsuperscript{186,187}. Similarly, while earlier studies of the capability of isotropic pair potentials to form a variety of crystal structures had been focused on isolated findings\textsuperscript{188}, recent studies have shown the acceleration of these investigations to screenings of increasingly large parameter spaces\textsuperscript{186,189}. Current efforts are further expanding these approaches to higher-dimensional searches\textsuperscript{190} powered by machine-learning-enabled methods\textsuperscript{191} and rendered possible by order parameters that permit the distinction of large varieties of crystal structures\textsuperscript{192,193}.

While it is challenging to investigate large swaths of parameter spaces or systems with many degrees of freedom via computation, this is even more true for experimental studies, where each synthesized system and each set of parameters requires a far deeper commitment of laboratory and human resources. Several studies have investigated the structure formation of large varieties of particles (e.g.,\textsuperscript{194}), and some have begun to derive predictive rules for the stabilization of different structures: for binary systems of DNA-functionalized nanoparticles, for example, a set of design rules pertaining to their relative sizes was expressed that predicted which crystal structure would form from them similar to Pauling’s rules for ionic compounds\textsuperscript{195}.

The interplay of the thermodynamics of a particle system—and therefore its underlying energy landscape—and the kinetic contributions that enable the actual assembly of a structure is intricate and presumably varies drastically between different physical systems. The larger length scales of mesoscopic particle systems, as compared with microscopic ones, lead to an increase in assembly timescales, which in computational approaches are intrinsically limited. As a result, factors of particle kinetics play an increasingly large role in determining which structures are observed, and therefore need to be taken into account explicitly (by simulating full assembly trajectories vs. comparing compound free energies) whenever possible. Polymorphism is a related obstacle, resulting from furrowed energy surfaces, i.e., the existence of multiple phases with competitive free energies, whose formation depends on assembly pathways, synthesis routes, and minute changes in crystal growth parameters. Here, too, the impact of kinetics has to be scrutinized in order to reliably document which circumstances lead to the assembly of a particular ordered structure.
ELUCIDATE AND DESCRIBE NEW CRYSTAL STRUCTURES

The exploration and discovery of new crystal structures in soft condensed matter must be paired with reliable means of structure determination as well as the reporting of crystal structures through a common language. The elucidation of crystal structures on the mesoscale has been under constant development, enabling the determination of structures via transmission electron microscopy with electron tomography,[192][193] and liquid cell transmission electron microscopy,[192] scanning probe microscopy and spectroscopy,[195] as well as scattering experiments.[196][198] In numerical simulations, structure determination is still mostly conducted on an ad-hoc basis and the development of more robust and versatile tools, as well as the incorporation of standard crystallographic techniques still lies ahead.

Another challenge to be tackled by the community is nomenclature: many of the known crystal structures are usually specified by a variety of names used for their hard-matter equivalents, ranging from prototypical compounds (“NaCl”), to the Strukturbericht designation (“A15 structure”) or other conventional descriptions originating from metallurgy (“σ phase”) or applied mathematics (“cubic-close packing”). When new structures are described, their characteristics are often put into context by using related and known crystal structures as proxies. Sometimes space groups are reported, which is extremely useful but does not define a unique crystal structure comprehensively. Additionally, Wyckoff positions as well as all free parameters (of the unit cell and of the particle coordinates) need to be specified in order to render a full description of a crystal structure.

Especially in referring to crystal structures via short designations, a large variety of nomenclatures have been employed, ranging from the previously mentioned manners of referring to known, atomic structures to very specific abbreviations that are laid out separately and from scratch for each new study. In recent years, we have promoted the use of the above-mentioned Pearson symbol to serve as an information-rich shorthand to refer to structures both new and previously known: the notation captures both the symmetry and complexity of a crystal structure—via the Bravais lattice and number of particles per unit cell—and simultaneously offers a more intuitive approach by linking these characteristics to a prototypical compound.

The last component of the Pearson notation—a structural prototype—points to a larger purpose, challenge, and opportunity of reporting crystal structures in the field of soft condensed matter: by finding a common language that is shared between the disciplines of materials science, chemical engineering, physics, and chemistry, our collective explorations in this interdisciplinary field can be communicated in ways that enable us to identify overarching principles—matching identical or similar structures in disparate systems or conditions.

One residual difficulty, however, is bound to persist despite the precise determination of particle positions and the adherence to a technically accurate structural description: the interpretation of crystal structures remains an ambiguous undertaking that relies on a correct abstraction of structural motifs and patterns. The meaning of structural models does not always transfer correctly between chemically distinct compounds—a condition that is inherently fulfilled in the length scale-spanning considerations in this manuscript. While the symmetry-based language to characterize fully ordered structures is precise, the geometrical description of crystal structures can remain ambiguous. One can therefore inadvertently sidestep the more important underlying question—beyond “where are the particles?”: “why are the particles arranged the way they are?”

CONCLUSIONS

Over the past few years, a growing number of increasingly complex crystal structures has been discovered on the mesoscale. Experimentation and computation have both rendered a diverse set of structures in a variety of systems and with many types of interactions. On the path toward making functional colloidal materials, advances will now increasingly require the dedicated design and synthesis of more structures, including new geometries that have no precedent on any materials length scale.

Simulation studies will need to stay ahead in their exploratory forays, to lighten the workload necessary for experimental studies through advancements in structure prediction, while also continually improving their relevance to physically meaningful interactions, and time scales. Experimentalists, on the other hand, are moving toward studies with higher throughput, while also expanding their methodological toolbox and the design dimensions along which the particles and their interactions can be tuned. By making headway in studies of both simulated and experimental systems, we will begin distilling a deeper understanding of when and how and why ordered crystals form from particles on the mesoscale. This will pave the way not just toward materials design of nano- and microstructured materials, but also a deeper understanding of emergent order and structure formation independent of length scale, broadening the impact of soft matter crystallography to become relevant for our understanding of atomistic crystallization and order.[203]

CITATION DIVERSITY STATEMENT

Recent work in several fields of science has identified a bias in citation practices such that papers from women
and other minority scholars are under-cited relative to the number of such papers in the field (e.g., 205–207). In order to provide transparency and accountability for citation gender imbalance, we used an open-source code that predicts the gender of the first and last author of each reference by using databases that store the probability of a first name being carried by a woman. Excluding self-citations, our references contain 8.18% woman/first)/woman/last), 15.67% man/woman, 10.09% woman/man, and 66.06% man/man by this measure. This method is limited in that (i) names, pronouns, and social media profiles used to construct the databases may not, in every case, be indicative of gender identity and (ii) it unfortunately cannot account for intersex, non-binary, or transgender people.

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DATA AVAILABILITY STATEMENT

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

AUTHOR DECLARATIONS

The author has no conflicts to disclose.

APPENDIX

The Pearson symbol is used throughout to denote crystal structure types. Its first component specifies a structure’s Bravais lattice, of which there are 14: $cF$ = face-centered cubic, $cI$ = body-centered cubic, $cP$ = primitive cubic, $hP$ = hexagonal, $hR$ = rhombohedral, $tI$ = body-centered tetragonal, $tP$ = primitive tetragonal, $oF$ = face-centered orthorhombic, $oI$ = body-centered orthorhombic, $oS$ = base-centered orthorhombic, $oP$ = primitive orthorhombic, $mS$ = base-centered monoclinic, $mP$ = primitive monoclinic, $aP$ = primitive triclinic.

The Bravais lattices are based on the 7 crystal systems:

- $c$ = cubic ($a = b = c$, $\alpha = \beta = \gamma = 90^\circ$),
- $b$ = hexagonal ($a = b$, $\alpha = \beta = \gamma = 90^\circ$, $\gamma = 120^\circ$),
- $t$ = tetragonal ($a = b$, $\alpha = \beta = \gamma = 90^\circ$),
- $o$ = orthorhombic ($\alpha = \beta = \gamma = 90^\circ$),
- $m$ = monoclinic ($\alpha = \gamma = 90^\circ$),
- $a$ = triclinic (no restrictions).

The lattice centering types indicate how many lattice points are contained in one unit cell and where these are located:

- $P$ = primitive (1 lattice point): $(0, 0, 0)$,
- $S$ = base-centered (2 lattice points): $(0, 0, 0)$ and either $(0, \frac{1}{2}, \frac{1}{2})$ (A) or $(\frac{1}{2}, 0, \frac{1}{2})$ (B) or $(\frac{1}{2}, \frac{1}{2}, 0)$ (C),
- $I$ = body-centered (2 lattice points): $(0, 0, 0)$ and $(1, \frac{1}{2}, \frac{1}{2})$,
- $F$ = face-centered (4 lattice points): $(0, 0, 0)$ and $(0, \frac{1}{2}, \frac{1}{2})$ and $(\frac{1}{2}, 0, \frac{1}{2})$ and $(\frac{1}{2}, \frac{1}{2}, 0)$,
- $R$ = rhombohedral (3 lattice points): $(0, 0, 0)$ and $(\frac{1}{3}, \frac{1}{3}, \frac{1}{3})$ and $(\frac{1}{3}, \frac{2}{3}, \frac{2}{3})$.

The number of atoms per unit cell given in the Pearson symbol refers to the indicated lattice centering and therefore does not necessarily correspond to the number of atoms per primitive unit cell (with the exception of the primitive Bravais lattices). All structures with rhombohedral space groups are given in their hexagonal setting.

Given below are several examples for how this notation operates. The diamond structure type $cF8-C$ has space group $Fd\bar{3}m$ (no. 227) with 8 atoms per unit cell, positioned on the Wyckoff site 8a which (in origin choice 2) corresponds to positions $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, as well as—due to the face-centered lattice, whose vectors have to be added to these coordinates in all combinations—$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. All of these positions are occupied by C atoms in the prototypical diamond phase.

The Frank-Kasper Z-phase structure type $hP7-Zr_4Al_3$ has space group $P6/mmm$ (no. 191) with 7 atoms per unit cell, positioned on Wyckoff sites 2c, which corresponds to positions $(\frac{1}{2}, \frac{1}{2}, 0)$ and $(\frac{1}{2}, \frac{1}{2}, 0)$; 2e, which corresponds to positions $(0, 0, z)$ and $(0, 0, z)$ (here with $z \approx 0.3$); and 3f, which corresponds to positions $(\frac{1}{2}, 0, 0)$, $(0, \frac{1}{2}, 0)$, and $(0, \frac{1}{2}, 0)$. In the prototypical compound $Zr_4Al_3$, sites 2c and 2e are occupied by Zr atoms, and site 3f is occupied by Al atoms. The aspect ratio of the unit cell of this structure type is $c/a \approx 1$.

The L1$_0$ structure type $tP2-CuAu$ has space group $P4/mmm$ (no. 123) with 2 atoms per unit cell, positioned on Wyckoff sites 1a, which corresponds to position $(0, 0, 0)$, and 1b, which corresponds to position $(0, 0, \frac{1}{2})$. In the prototypical compound $CuAu$, site 1a is occupied by Au atoms and site 1b is occupied by Cu atoms. The aspect ratio of the unit cell of this structure type is $c/a \approx 1.3$. (“L1$_0$” is a “Strukturbericht” designation for intermetallic compounds.)

REFERENCES

1. David B. Lukatsky, B. M. Mulder, and Daan Frenkel. Designing ordered DNA-linked nanoparticle assemblies. Journal of Physics: Condensed Matter, 18:5567–5580, 2006.
2. Michael A. Boles, Michael Engel, and Dmitri V. Talapin. Self-Assembly of Colloidal Nanocrystals: From Intricate Structures to Functional Materials. Chemical Reviews, 116:11220–11289, 2016.
3 Walter Steurer and Sofia Deloudi. *Crystallography of quasicrystals: concepts, methods and structures*. Springer Series in Materials Science, 2009.

4 Julia Dhemuchadse and Walter Steurer. On the Symmetry and Composition of Complex Intermetallics. *MRS Proceedings*, 1517:msf12–1517–kbo1–01, 2012.

5 Amir Haji-Akbari, Michael Engel, Aaron S. Keys, Xiaooyu Zheng, Rolle G. Petschek, Peter Palfly-Muhoray, and Sharon C. Glotzer. Disordered, quasicrystalline and crystalline phases of densely packed tetrahedra. *Nature*, 462:773–777, 2009.

6 Michael Engel, Pablo F. Damasceno, Carolyn L. Phillips, and Sharon C. Glotzer. Computational self-assembly of a one-component icosahedral quasicrystal. *Nature Materials*, 14(1):109–116, 2015.

7 Sharon C. Glotzer and Michael J. Solomon. Anisotropy of Building Blocks and Their Assembly into Complex Structures. *Nature Materials*, 6(7):557–562, 2007.

8 Greg van Anders, N. Khalid Ahmed, Ross Smith, Michael Engel, and Sharon C. Glotzer. Entropically Patchy Particles: Engineering Valence through Shape Envelope. *ACS Nano*, 8(1):931–940, 2014.

9 Rudolf Allmann and Roland Hinek. The introduction of structure types into the Inorganic Crystal Structure Database ICSD. *Acta Crystallographica A*, 63:412–417, 2007.

10 Pierre Villars and Karin Cenzual. Pearson’s Crystal Data: Crystal Structure Database for Inorganic Compounds. https://www.crystalimpact.com/pcd/, 2020.

11 Sergey Krivovichev. Topological complexity of crystal structures: quantitative approach. *Acta Crystallographica A*, 68:393–398, 2012.

12 Sergey V. Krivovichev. Which Inorganic Structures are the Most Complex? *Angewandte Chemie International Edition*, 53:654–661, 2014.

13 UICr. Report of the Executive Committee for 1991. *Acta Crystallographica A*, 48:922–946, 1992.

14 Ted Janssen, Gervais Chapuis, and Marc de Boissieu. Aperiodic Crystals – From Modulated Phases to Quasicrystals, volume 20 of UICr Monographs on Crystallography. Oxford University Press, 2007.

15 Sander van Smaalen. *Incommensurate Crystallography*, volume 21 of UICr Monographs on Crystallography. Oxford University Press, 2007.

16 Thomas Richard Welberry. *Diffuse X-Ray Scattering and Models of Disorder*, volume 16 of UICr Monographs on Crystallography. Oxford University Press, 2010.

17 David A. Keen and Andrew L. Goodwin. The crystallography of correlated disorder. *Nature*, 521:303–309, 2015.

18 Arkady Simonov and Andrew L. Goodwin. Designing disorder into crystalline materials. *Nature Reviews Chemistry*, 4:657–673, 2020.

19 Dejan Zagorac, H. Müller, S. Ruehl, Julena Zagorac, and Silke Rehme. Recent developments in the Inorganic Crystal Structure Database: theoretical crystal structure data and related features. *Journal of Applied Crystallography*, 52:918–925, 2019.

20 Julia Dhemuchadse and Walter Steurer. Some Statistics on Intermetallic Compounds. *Inorganic Chemistry*, 54(3):1120–1128, 2015.

21 Sten Samson. Crystalline Structure of NaCd₂. *Nature*, 195(4838):259–262, 1962.

22 Sten Samson. The Crystal Structure of the Phase β Mg₂Al₃. *Acta Crystallographica*, 19:401–413, 1965.

23 Sten Samson. The Crystal Structure of the Intermetallic Compound Cu₄Cd₃. *Acta Crystallographica*, 23:586–600, 1967.

24 Thomas Weber, Julia Dhemuchadse, Miroslav Kobas, Matthias Conrad, Bernd Harbrecht, and Walter Steurer. Large, larger, largest – a family of cluster-based tantalum copper aluminides with giant unit cells. I. Structure solution and refinement. *Acta Crystallographica B*, 65:308–317, 2009.

25 Matthias Conrad, Bernd Harbrecht, Thomas Weber, Daniel Y. Jung, and Walter Steurer. Large, larger, largest – a family of cluster-based tantalum copper aluminides with giant unit cells. II. The cluster structure. *Acta Crystallographica B*, 65:318–325, 2009.

26 Julia Dhemuchadse, Daniel Y. Jung, and Walter Steurer. Structural building principles of complex face-centered cubic intermetallics. *Acta Crystallographica B*, 67:28–292, 2011.

27 Dan Shechtman, I. Blech, D. Gratias, and John W. Cahn. Metallic Phase with Long-Range Orientational Order and No Translational Symmetry. *Physical Review Letters*, 53(20):1951–1953, 1984.

28 Walter Steurer. Quasicrystals: What do we know? What do we want to know? What can we know? *Acta Crystallographica A*, 74:1–11, 2018.

29 Stefan Förster, Klaus Meinel, René Hammer, Martin Trautmann, and Wolf Wildra. Quasicrystalline structure formation in a classical crystalline thin-film system. *Nature*, 502:215–218, 2013.

30 Eva Maria Zollner, Sebastian Schenk, Martin Setvin, and Stefan Förster. Perfect Monolayers of the BaTiO₃-Derived 2D Oxide Quasicrystals Investigated by Scanning Tunneling Microscopy and Noncontact Atomic Force Microscopy. *Physica Status Solidi B*, 257:1900620, 2020.

31 Indu Bhusan Sharma and Devinder Singh. Solid state chemistry of Ruddlesden-Popper type complex oxides. *Bulletin of Materials Science*, 21(5):363–374, 1998.

32 Lynne B. McCusker and Christian Baerlocher. Zeolite Structures. In Jiří Čejka, Herman van Bekkum, Avelino Corma, and Ferdi Schüth, editors, *Introduction to Zeolite Science and Practice*, volume 168, chapter 2, pages 13–103. Elsevier, 3rd edition, 2007.

33 Christian Baerlocher, Lynne B. McCusker, and David H. Olson. Atlas of Zeolite Framework Types. Elsevier Science, 6th edition, 2007.

34 Structure Commission of the International Zeolite Association. Database of Zeolite Structures. http://www.iza-structure.org/databases/, 2020.

35 David J. Earl and Michael W. Deem. Toward a Database of Hypothetical Zeolite Structures. *Industrial & Engineering Chemistry Research*, 45:5449–5454, 2006.

36 Jiyang Li, Avelino Corma, and Jihong Yu. Synthesis of new zeolite structures. *Chemical Society Reviews*, 44:7112–7127, 2015.

37 Michael Baittinger, Bodo Böhme, Alim Ormeci, and Yuri Grin. Solid State Chemistry of Clathrate Phases: Crystal Structure, Chemical Bonding and Preparation Routes. In G S Nolas, editor, *Phys. Chem. Inorg. Clathrates*, volume 199 of *Springer Series in Materials Science*, chapter 2, pages 35–64. Springer Science+Business Media, 2014.

38 Linus Pauling and Richard E. Marsh. The Structure of Chlorine Hydrate. *Proc. Natl. Acad. Sci.*, 38:112–118, 1952.

39 Michael O’Keeffe and Omar M. Yaghi. Deconstructing the Crystal Structures of Metal–Organic Frameworks and Related Materials into Their Underlying Nets. *Chemical Reviews*, 112(2):675–702, 2012.

40 Adrien P. Côté, Annabelle I. Benin, Nathan W. Ockwig, Michael O’Keeffe, Adam J. Matzger, and Omar M. Yaghi. Porous, Crystaline, Covalent Organic Frameworks. *Science*, 310(5751):1166–1170, 2005.

41 William W. Wood and Jack D. Jacobson. Preliminary Results for a Hard Sphere System. *The Journal of Chemical Physics*, 27:1207–1208, 1957.

42 Berni J. Alder and Thomas E. Wainwright. Phase Transition for a Hard Sphere System. *The Journal of Chemical Physics*, 27:1208–1209, 1957.

43 Peter N. Pusey, W. van Megen, P. Bartlett, B. J. Ackerson, J. G. Rarity, and Sonia M. Underwood. Structure of Crystals of Hard Colloidal Spheres. *Physical Review Letters*, 63(25):2753–2756, 1989.

44 Jixiang Zhu, Min Li, R. Rogers, W. Meyer, R. H. Ottewill, STS-73 Space Shuttle Crew, W. B. Russel, and Paul M. Chaikin.
Crystallization of hard-sphere colloids in microgravity. *Nature*, 387:883–885, 1997.

45 Robert J. Macfarlane, Matthew R. Jones, Andrew J. Senesi, Kaylle L. Young, Byeongyu Lee, Jinsong Wu, and Chad A. Mirkin. Establishing the Design Rules for DNA-Mediated Programmable Colloidal Crystallization. *Angewandte Chemie International Edition*, 49:4589–4592, 2010.

46 Robert J. Macfarlane, Byeongyu Lee, Matthew R. Jones, Nandine Harris, George C. Schatz, and Chad A. Mirkin. Nanoparticle Superlattice Engineering with DNA. *Science*, 334:204–208, 2011.

47 Elena V. Shevchenko, Dmitri V. Talapin, Nicholas A. Kotov, Stephen O’Brien, and Christopher B. Murray. Structural diversity in binary nanoparticle superlattices. *Nature*, 439:55–59, 2006.

48 CrystalMaker Software Ltd, Oxford, England. *CrystalMaker®: a crystal and molecular structures program for Mac and Windows*, 2021.

49 Pablo F. Damasceno, Michael Engel, and Sharon C. Glotzer. Predictive self-assembly of polyhedra into complex structures. *Science*, 337(6093):453–457, 2012.

50 Ryan L. Marson, Erin G. Teich, Julia Dshemuchadse, Sharon C. Glotzer, and Ronald G. Larson. Computational self-assembly of colloidal crystals from Platonic polyhedral sphere clusters. *Soft Matter*, 15:6288–6299, 2019.

51 Joel Henzie, Michael Grünwald, Asaph Widmer-Cooper, Phillip L. Geissler, and Peidong Yang. Self-assembly of uniform polyhedral silver nanocrystals into densest packings and exotic superlattices. *Nature Materials*, 11:131–137, 2012.

52 Sangwoo Lee, Michael J. Blumentle, and Frank S. Bates. Discovery of a Frank-Kasper \( \sigma \) Phase in Sphere-Forming Block Copolymer Melts. *Science*, 330:349–353, 2010.

53 Sangwoo Lee, Chris Leighton, and Frank S. Bates. Sphericity and symmetry breaking in the formation of Frank-Kasper phases from one component materials. *Proceedings of the National Academy of Sciences*, 111:17723–17731, 2014.

54 Siddharth Chauanpuriya, Kyungtae Kim, Jingwen Zhang, Sangwoo Lee, Akash Arora, Kevin D. Dorfman, Kris T. Delaney, Glenn H. Fredrickson, and Frank S. Bates. Cornucopia of Nanoscale Ordered Phases in Sphere-Forming Tetrablock Terpolymers. *ACS Nano*, 10:4961–4972, 2016.

55 Kan Yue, Mingjun Huang, Ryan L. Marson, Jinlin He, Jiahao Huang, Zhe Zhou, Jing Wang, Chang Liu, Xuesheng Yan, Kan Wu, Zaihong Guo, Hao Liu, Wei Zhang, Peihong Ni, Chrys Wesdemiotis, Wen-Bin Zhang, Sharon C. Glotzer, and Stephen Z. D. Cheng. Geometry induced sequence of nanoscale Frank–Kasper and quasicrystal mesophases in giant surfactants. *Proceedings of the National Academy of Sciences*, 113:14195–14200, 2016.

56 Sung A. Kim, Kyeeong-Jun Jeong, Arun Yethiraj, and Marc A. Hillmyer. Inverse Design of Self-Assembling Frank-Kasper Phases and Insights Into Emergent Quasicrystals. *The Journal of Physical Chemistry B*, 122:5547–5556, 2018.

57 Morgan W. Schulze, Ronald M. Lewis, James H. Lettow, Robert J. Hickey, Timothy M. Gillard, Marc A. Hillmyer, and Frank S. Bates. Conformational Asymmetry and Quasicrystal Approximants in Linear Diblock Copolymers. *Physical Review Letters*, 118:207801, 2017.

58 Zebin Su, Chih-Hao Hsu, Zihao Gong, Xueyan Feng, Jiahao Huang, Ruimeng Zhang, Yu Wang, Jinlai Mao, Chrys Wesdemiotis, Tao Li, Soenke Seifert, Wei Zhang, Takuzo Aida, Mingjun Huang, and Stephen Z. D. Cheng. Identification of a Frank–Kasper \( \kappa \) phase from shape amphiilibale self-assembly. *Nature Chemistry*, 11:899–905, 2019.

59 Steffen Fischer, Alexander Exner, Kathrin Zieslkes, Jan Perlich, Sofia Deokoul, Walter Steurer, Peter Lindner, and Stephan Förster. Colloidal quasicrystals with 12-fold and 18-fold diffraction symmetry. *Proceedings of the National Academy of Sciences*, 108(5):1810–1814, 2011.

60 Dmitri V. Talapin, Elena V. Shevchenko, Maryna I. Bodnar-chuk, Xingchen Ye, Jun Chen, and Christopher B. Murray. Quasicrystalline order in self-assembled binary nanoparticle superlattices. *Nature*, 461:964–967, 2009.

61 Xingchen Ye, Jun Chen, Eric Irgang, Michael Engel, Ang-gang Dong, Sharon C. Glotzer, and Christopher B. Murray. Quasicrystalline nanocrystal superlattice with partial matching rules. *Nature Materials*, 16:214–219, 2017.

62 Jingwen Zhang and Frank S. Bates. Dodecagonal Quasicrystalline Morphology in a Poly(styrene-b-isooprene-b-styrene-b-ethylene oxide) Tetrablock Terpolymer. *Journal of the American Chemical Society*, 134:7636–7639, 2012.

63 Xiangbing Zeng, Goran Ungar, Yongsong Liu, Virgil Percce, Andrés E. Dulcey, and Jamie K. Hobbs. Supramolecular dendritic liquid quasicrystals. *Nature*, 428:157–160, 2004.

64 Tomonari Dotera, T. Oshiro, and Primoz Ziherl. Mosaic two-dendric liquid quasicrystals. *Nature Chemistry*, 439:55–59, 2000.

65 Tomonari Dotera, T. Oshiro, and Primoz Ziherl. Mosaic two-dendric liquid quasicrystals. *Nature Chemistry*, 439:55–59, 2000.

66 Fredrik H. M. Zetterling, Mikhail Dzugutov, and Sven Lidin. \( \gamma \)-Brass Crystallization in a Simple Monotonic Liquid. *MRS Proceedings*, 643:E9.5, 2000.

67 Måns Elenius, Fredrik H. M. Zetterling, Mikhail Dzugutov, Daniel C. Fredrickson, and Sven Lidin. Structural model for octagonal quasicrystals derived from octagonal symmetry elements arising in \( \beta \)-Mo crystallization of a simple monotonic liquid. *Physical Review B*, 79(14):144201, 2009.

68 Praveen K. Bommenneni, Nydia Roxana Varela-Rosales, Marco Klement, and Michael Engel. Complex Crystals from Size-
Disperse Spheres. *Physical Review Letters*, 122:128005, 2019.

79 Yufeng Wang, Yu Wang, Xiaolong Zheng, Etienne Ducrot, Myung-Goo Lee, Gi-Ra Yi, Marcus Weck, and David J. Pine. Synthetic Strategies Toward DNA-Coated Colloids that Crystallize. *Journal of the American Chemical Society*, 137:10760-10766, 2015.

80 Wiel H. Evers, Heiner Friedrich, Laura Filion, Marjolein Dijkstra, and Daniel Vanmaekelbergh. Observation of a Ternary Nanocrystal Superlattice and Its Structural Characterization by Electron Tomography. *Angewandte Chemie International Edition*, 48:9655-9657, 2009.

81 Xingchen Ye, Jun Chen, and Christopher B. Murray. Polymorphism in Self-Assembled Aβ₆ Binary Nanocrystal Superlattices. *Journal of the American Chemical Society*, 133:2613-2620, 2011.

82 Alexei V. Tkachenko. Morphological Diversity of DNA-Colloidal Self-Assembly. *Physical Review Letters*, 89(14):148303, 2002.

83 Petr Cigler, Abigail K. R. Lytton-Jean, Daniel G. Anderson, M. G. Finn, and Sung Yong Park. DNA-controlled assembly of a NaTL lattice structure from gold nanoparticles and protein nanoparticles. *Nature Materials*, 9:918-922, 2010.

84 Yifan Wang, Ian C. Jenkins, James T. McGинley, Talid Sinno, and John C. Crocker. Colloidal crystals with diamond symmetry at optical lengthscales. *Nature Communications*, 8:14173, 2017.

85 Andrew T. Cadotte, Julia Dshemuchadse, Pablo F. Damasceno, Richmond S. Newman, and Sharon C. Glotzer. Self-assembly of a space-tessellating structure in the binary system of hard tetrahedra and octahedra. *Soft Matter*, 12(34):7073-7078, 2016.

86 Mehdi B. Zanjani, Ian C. Jenkins, John C. Crocker, and Talid Sinno. Colloidal Cluster Assembly into Ordered Superstructures via Engineered Directional Binding. *ACS Nano*, 10:11280-11289, 2016.

87 Laura Rossi, Stefano Sacanna, William T. M. Irvine, Paul M. Chaikin, David J. Pine, and Albert P. Philipse. Cubic crystals from cubic colloids. *Soft Matter*, 7:4139-4142, 2011.

88 Mikael C. Rechtsman, Frank H. Stillinger, and Salvatore Torquato. Self-assembly of the simple cubic lattice with an isotropic potential. *Physical Review E*, 74:021144, 2006.

89 Avni Jain, Jeffrey R. Errington, and Thomas M. Truskett. Communication: Phase behavior of materials with isotropic interactions designed by inverse strategies to favor diamond and simple cubic lattice ground states. *Journal of Chemical Physics*, 139:141102, 2013.

90 Robin van Damme, B. van der Meer, J. J. van den Broeke, F. Smallenburg, and Laura Filion. Phase and vacancy behaviour of hard “slanted” cubes. *The Journal of Chemical Physics*, 147:124501, 2017.

91 Pablo F. Damasceno, Michael Engel, and Sharon C. Glotzer. Crystalline Assemblies and Dense Packings of a Family of Truncated Tetrahedra and the Role of Directional Entropic Forces. *ACS Nano*, 6(1):690-614, 2012.

92 Mingxin He, Johnathon P. Gales, Étienne Ducrot, Zhe Gong, Gi-Ra Yi, Stefano Sacanna, and David J. Pine. Colloidal diamond. *Nature*, 585:524-529, 2020.

93 Mikael C. Rechtsman, Frank H. Stillinger, and Salvatore Torquato. Synthetic diamond and wurtzite structures regarded as sphere packings. I. Definitions and basic principles. *Acta Crystallographica*, C 13(3):181-190, 1958.

94 Amber S. Frank and John S. Kasper. Complex alloy structures regarded as sphere packings. II. Classification and classification of representative structures. *Acta Crystallographica*, 12(7):483-499, 1959.

95 Alex Travesset. Nanoparticle Superlattices as Quasi-Frank-Kasper Phases. *Physical Review Letters*, 119:115701, 2017.

96 Abhiram Reddy and Gregory M. Grason. A cornerstone of complex crystals. *Nature Chemistry*, 11:865-867, 2019.

97 Andrew T. Cadotte, Julia Dshemuchadse, Pablo F. Damasceno, Michael Engel, and Sharon C. Glotzer. Understanding shape entropy of hard “slanted” cubes. *Science*, 137:10760-10766, 2010.

98 Eric S. Harper, Greg van Anders, and Sharon C. Glotzer. Programmable self-assembly of diamond polymorphs from chromatic patchy particles. *Physical Review E*, 98:032611, 2018.

99 Matthew Spillings and Sharon C. Glotzer. Machine Learning for Crystal Identification and Discovery. *AIChe Journal*, 64(6):2198-2206, 2018.

100 Eva G. Noya, Itziar Zubieta, David J. Pine, and Francesco Sciortino. Assembly of clathrates from tetrahedral patchy colloids with narrow patches. *The Journal of Chemical Physics*, 151:094502, 2019.

101 Sangmin Lee, Eric G. Teich, Michael Engel, and Sharon C. Glotzer. Entropic colloidal crystallization pathways via fluid-fluid transitions and multidimensional pre nucleation motifs. *Proceedings of the National Academy of Sciences*, 116(30):14843-14851, 2019.

102 Frederick C. Frank and John S. Kasper. Complex alloy structures regarded as sphere packings. I. Definitions and basic principles. *Acta Crystallographica*, 11(3):84-190, 1958.

103 Frickel C. Frank and John S. Kasper. Complex alloy structures regarded as sphere packings. II. Analysis and classification of representative structures. *Acta Crystallographica*, 12(7):483-499, 1959.

104 Alex Travesset. Nanoparticle Superlattices as Quasi-Frank-Kasper Phases. *Physical Review Letters*, 119:115701, 2017.

105 Abhiram Reddy and Gregory M. Grason. A cornerstone of complex crystals. *Nature Chemistry*, 11:865-867, 2019.

106 Andrew T. Cadotte, Julia Dshemuchadse, Pablo F. Damasceno, Michael Engel, and Sharon C. Glotzer. Understanding shape entropy of hard “slanted” cubes. *Science*, 137:10760-10766, 2010.

107 Andrew T. Cadotte, Julia Dshemuchadse, Pablo F. Damasceno, Michael Engel, and Sharon C. Glotzer. Understanding shape entropy of hard “slanted” cubes. *Science*, 137:10760-10766, 2010.

108 Andrew T. Cadotte, Julia Dshemuchadse, Pablo F. Damasceno, Michael Engel, and Sharon C. Glotzer. Understanding shape entropy of hard “slanted” cubes. *Science*, 137:10760-10766, 2010.

109 Andrew T. Cadotte, Julia Dshemuchadse, Pablo F. Damasceno, Michael Engel, and Sharon C. Glotzer. Understanding shape entropy of hard “slanted” cubes. *Science*, 137:10760-10766, 2010.

110 Andrew T. Cadotte, Julia Dshemuchadse, Pablo F. Damasceno, Michael Engel, and Sharon C. Glotzer. Understanding shape entropy of hard “slanted” cubes. *Science*, 137:10760-10766, 2010.

111 Andrew T. Cadotte, Julia Dshemuchadse, Pablo F. Damasceno, Michael Engel, and Sharon C. Glotzer. Understanding shape entropy of hard “slanted” cubes. *Science*, 137:10760-10766, 2010.

112 Andrew T. Cadotte, Julia Dshemuchadse, Pablo F. Damasceno, Michael Engel, and Sharon C. Glotzer. Understanding shape entropy of hard “slanted” cubes. *Science*, 137:10760-10766, 2010.

113 Andrew T. Cadotte, Julia Dshemuchadse, Pablo F. Damasceno, Michael Engel, and Sharon C. Glotzer. Understanding shape entropy of hard “slanted” cubes. *Science*, 137:10760-10766, 2010.

114 Andrew T. Cadotte, Julia Dshemuchadse, Pablo F. Damasceno, Michael Engel, and Sharon C. Glotzer. Understanding shape entropy of hard “slanted” cubes. *Science*, 137:10760-10766, 2010.
tity crisis in alchemical space drives the entropic colloidal glass transition. Nature Communications, 10:64, 2019.

118 Rose K. Cersonsky, Julia Dshemuchadse, James Antonaglia, Greg van Anders, and Sharon C. Glotzer. Pressure-tunable photonic band gaps in an entropic colloidal crystal. Physical Review Materials, 2:0125201, 2018.

119 Chrisy Xiyu Du, Greg van Anders, Richmond S. Newman, and Sharon C. Glotzer. Shape-driven solid–solid transitions in colloids. Proceedings of the National Academy of Sciences, 114:E3892–E3899, 2017.

120 Chrisy Xiyu Du, Greg van Anders, Julia Dshemuchadse, Paul M. Dodd, and Sharon C. Glotzer. Inverse design of compression-induced solid–solid transitions in colloids. Molecular Simulation, 46(14):1037–1044, 2020.

121 Vikram Thapar and Fernando A. Escobedo. Localized Orien-
tational Order Chaperones the Nucleation of Rotator Phases in Hard Polyhedral Particles. Physical Review Letters, 112:048301, 2014.

122 Abhishek K. Sharma, Vikram Thapar, and Fernando A. Escobedo. Solid-phase nucleation free-energy barriers in truncated cubes: interplay of localized orientational order and facet alignment. Soft Matter, 14:1996–2005, 2018.

123 Richmond S. Newman, Samantha Nola, Julia Dshemuchadse, and Sharon C. Glotzer. Shape-controlled crystallisation pathways in dense fluids of ccp-forming hard polyhedra. Molecular Physics, 117(23-24):3819–3826, 2019.

124 Bettina S. John, Abraham Stroock, and Fernando A. Escobedo. Cubatic liquid-crystalline behavior in a system of hard cuboids. Journal of Chemical Physics, 120(19):9383–9389, 2004.

125 Umang Agarwal and Fernando A. Escobedo. Mesophase behav-
ior of polyhedral particles. Nature Materials, 10:230–235, 2011.

126 Andrew S. Karas, Julia Dshemuchadse, Greg van Anders, and Sharon C. Glotzer. Phase behavior and design rules for plastic colloidal crystals of hard polyhedra via consideration of directional entropic forces. Soft Matter, 15(27):5380–5389, 2019.

127 Abhishek K. Sharma and Fernando A. Escobedo. Disorder Fore-
shadowing Order in Colloidal Cubes. The Journal of Physical Chemistry B, 122:9264–9273, 2018.

128 Abhiram Reddy, Michael B. Buckley, Akash Arora, Frank S. Bates, and Kevin D. Dorfmanand Gregory M. Grason. Stable Frank–Kasper phases of self-assembled, soft matter spheres. Proceedings of the National Academy of Sciences, 115(41):10233–10238, 2018.

129 Christos N. Likos, Hartmut Löwen, Martin Watzlawek, B. Abbas, O. Jucknischke, J. Allgaier, and Dieter Richter. Star Poly-
mers Viewed as Ultrasoft Colloidal Particles. Physical Review Letters, 80(20):4450–4453, 1998.

130 Ard A. Louis, Peter G. Bolhuis, J. P. Hansen, and Evert J. Meijer. Can Polymer Coils Be Modeled as “Soft Coils”? Physical Review Letters, 85(12):2522–2525, 2000.

131 Peter G. Bolhuis, Ard A. Louis, J. P. Hansen, and Evert J. Meijer. Accurate effective pair potentials for polymer solutions. Journal of Chemical Physics, 114(9):4296–4311, 2001.

132 Christos N. Likos. Soft matter with soft particles. Soft Matter, 2:478–498, 2006.

133 Jean-Louis Bretonnet. Competing interactions in colloidal sus-
2007.

134 Nathan Horst and Alex Travesset. Prediction of binary nanoparticle superlattices from soft potentials. The Journal of Chemical Physics, 144:014502, 2016.

135 Alex Travesset. Topological structure prediction in binary nanoparticle superlattices. Soft Matter, 13:147–157, 2017.

136 R. Allen LaCour, Carl Simon Ador, Julia Dshemuchadse, and Sharon C. Glotzer. Influence of Softness on the Stability of Binary Colloidal Crystals. ACS Nano, 13:13829–13842, 2019.

137 Shang Ren, Yang Sun, Feng Zhang, Alex Travesset, Cai-Zhuang Zhong-Yuan Lu, and Zhao-Yan Sun. Softness-Enhanced Self-
assembly of Pyrochlore- and Perovskite-like Colloidal Photonic Superlattices from a Lennard-Jones Model. ACS Nano, 14:6795–6802, 2020.

138 Mark P. Boneschanscher, Wieh H. Evers, Weikai Qi, Johannes D. Meeldijk, Marjolein Dijkstra, and Daniel Vanmaekelbergh. Electron Tomography Resolves a Novel Crystal Structure in a Binary Nanocrystal Superlattice. Nano Letters, 13:1312–1316, 2013.

139 Elena V. Shevchenko, Dmitri V. Talapin, Stephen O’Brien, and Christopher B. Murray. Polymorphism in AIB3 Nanoparticle Superlattices: An Example of Semiconductor–Metal Metamaterials. Journal of the American Chemical Society, 127:8741–8747, 2005.

140 Haixin Lin, Sangmin Lee, Lin Sun, Matthew Spellings, Michael Engel, Sharon C. Glotzer, and Chad A. Mirkin. Clathrate col-
loidal crystals. Science, 355:931–935, 2017.

141 Zhan-Wei Li, Yu-Wei Sun, Yan-Hui Wang, You-Liang Zhu, Zhong-Yuan Lu, and Zhao-Yan Sun. Softness-Enhanced Self-
assembly of Pyrochlore- and Perovskite-like Colloidal Photonic Crystals from Triblock Janus Particles. The Journal of Physical Chemistry Letters, 12(30):7159–7165, 2021.

142 Harini Pattabhiraman, Guido Avvisati, and Marjolein Dijkstra. Novel Pyrochlorelike Crystal with a Photonic Band Gap Self-
Assembled Using Colloids with a Simple Interaction Potential. Physical Review Letters, 119:157401, 2017.

143 Uri R. Gabinet and Chinedum O. Osuji. Optical materials and metamaterials from nanostructured soft matter. Nano Research, 12(9):2172–2183, 2019.

144 Ian D. Hosein, Stephanie H. Lee, and Cheksha M. Liddell. Dimer-Based Three-Dimensional Photonic Crystals. Advanced Functional Materials, 20:3085–3091, 2010.

145 Ian D. Hosein, M. Ghebrebrhan, J. D. Joannopoulos, and Cheke-
sha M. Liddell. Dimer Shape Anisotropy: A Nonspherical Colloidal Approach to Omnidirectional Photonic Band Gaps. Lang-
muir, 26(3):2151–2159, 2010.

146 Esther Y. K. Fung, Kullachate Muangnapoh, and Cheksha M. Liddell Watson. Anisotropic photonic crystal building blocks: colloids tuned from mushroom-caps to dimers. Journal of Materials Chemistry, 22:10507–10513, 2012.

147 Erin K. Riley, E. Y. Fung, and Cheksha M. Liddell Wat-

148 Shang Ren, Yang Sun, Feng Zhang, Alex Travesset, Cai-Zhuang Zhong-Yuan Lu, and Zhao-Yan Sun. Softness-Enhanced Self-
assembly of Pyrochlore- and Perovskite-like Colloidal Photonic Superlattices from a Lennard-Jones Model. ACS Nano, 14:6795–6802, 2020.

149 Mark P. Boneschanscher, Wieh H. Evers, Weikai Qi, Johannes D. Meeldijk, Marjolein Dijkstra, and Daniel Vanmaekelbergh. Electron Tomography Resolves a Novel Crystal Structure in a Binary Nanocrystal Superlattice. Nano Letters, 13:1312–1316, 2013.

150 Elenav Shevchenko, Dmitri V. Talapin, Stephen O’Brien, and Christopher B. Murray. Polymorphism in AIB3 Nanoparticle Superlattices: An Example of Semiconductor–Metal Metamaterials. Journal of the American Chemical Society, 127:8741–8747, 2005.

151 Haixin Lin, Sangmin Lee, Lin Sun, Matthew Spellings, Michael Engel, Sharon C. Glotzer, and Chad A. Mirkin. Clathrate collo-
loidal crystals. Science, 355:931–935, 2017.

152 Zhan-Wei Li, Yu-Wei Sun, Yan-Hui Wang, You-Liang Zhu, Zhong-Yuan Lu, and Zhao-Yan Sun. Softness-Enhanced Self-
assembly of Pyrochlore- and Perovskite-like Colloidal Photonic Crystals from Triblock Janus Particles. The Journal of Physical Chemistry Letters, 12(30):7159–7165, 2021.

153 Harini Pattabhiraman, Guido Avvisati, and Marjolein Dijkstra. Novel Pyrochlorelike Crystal with a Photonic Band Gap Self-
Assembled Using Colloids with a Simple Interaction Potential. Physical Review Letters, 119:157401, 2017.

154 Uri R. Gabinet and Chinedum O. Osuji. Optical materials and metamaterials from nanostructured soft matter. Nano Research, 12(9):2172–2183, 2019.

155 Ian D. Hosein, Stephanie H. Lee, and Cheksha M. Liddell. Dimer-Based Three-Dimensional Photonic Crystals. Advanced Functional Materials, 20:3085–3091, 2010.

156 Ian D. Hosein, M. Ghebrebrhan, J. D. Joannopoulos, and Cheke-
sha M. Liddell. Dimer Shape Anisotropy: A Nonspherical Colloidal Approach to Omnidirectional Photonic Band Gaps. Lang-
muir, 26(3):2151–2159, 2010.

157 Esther Y. K. Fung, Kullachate Muangnapoh, and Cheksha M. Liddell Watson. Anisotropic photonic crystal building blocks: colloids tuned from mushroom-caps to dimers. Journal of Materials Chemistry, 22:10507–10513, 2012.
Buckled colloidal crystals with nonspherical bases for two-dimensional slab photonic band gaps. *Journal of Applied Physics*, 111:093504, 2012.

158 Angela C. Stelson, Erin K. Riley, and Chekesha M. Liddell Watson. Complete photonic band gaps in self-assembled square bilayer structures. *Journal of the Optical Society of America B*, 33(8):1588–1593, 2016.

159 Angela C. Stelson, Wesley A. Britton, and Chekesha M. Liddell Watson. Photonic crystal properties of self-assembled Archimedean tilings. *Journal of Applied Physics*, 121:023101, 2017.

160 Seokhyoung Kim, Cindy Y. Zheng, George C. Schatz, Koray Aydin, Kyoung-Ho Kim, and Chad A. Mirkin. Mie-Resonant Three-Dimensional Metacrystals. *Nano Letters*, 20:8960–8961, 2020.

161 Emanuele Marino, Alice Sciortino, Annemarie Berkhourt, Katherine E. MacArthur, Marc Heggen, Tom Gregorkiewicz, Thomas E. Kodger, Antonio Capretti, Christopher B. Murray, A. Fermi Koenderink, Fabrizio Messina, and Peter Schall. Simultaneous Photonic and Exciton Coupling in Spherical Quantum Dot Supercrystals. *ACS Nano*, 14:13806–13815, 2020.

162 Marius Schötte, Thomas Tran, Tanja Feller, and Markus Rettsch. Time–Temperature Integrating Optical Sensors Based on Gradient Colloidal Crystals. *Advanced Materials*, early view:2101948, 2021.

163 Mehdi B. Zanjani and Jennifer R. Lukes. Shape- and Structure-Based Phonon Bandgap Tuning with NanoCrystal Superlattices. *The Journal of Physical Chemistry C*, 119:16889–16896, 2015.

164 Kiumars Aryana and Mehdi B. Zanjani. Diamond family of colloidal supercrystals as phononic metamaterials. *Journal of Applied Physics*, 123:185103, 2018.

165 Caroline L. Poyser, Thomas Cserniuk, Andrey Akimov, Benjamin T. Diroll, E. Adeleye Golding, Alexey S. Salasyuk, Anthony J. Kent, Dmitri R. Yakovlev, Manfred Bayer, and Christopher B. Murray. Coherent Acoustic Phonons in Colloidal Semiconductor Nanocrystal Superlattices. *ACS Nano*, 10,1163–1169, 2016.

166 Douglas L. Medlin and G. Jeffrey Snyder. Interfaces in bulk thermoelastic materials: A review for Current Opinion in Colloid and Interface Science. *Current Opinion in Colloid & Interface Science*, 14:226–235, 2009.

167 Maksym V. Kovalenko, Liberato Manna, Andreu Cabot, Zeger Hens, Dmitri V. Talapin, Cherie R. Kagan, Victor I. Klimov, Andrey L. Rogach, Peter Reiss, Delia J. Milliron, Philippe Guyot-Sionnest, Gerasimos Konstantatos, Wolfgang J. Parak, Tai-hwan Yeon, Brian A. Korgel, Christopher B. Murray, and Wolfgang Heiss. Prospects of Nanoscience with Nanocrystals. *ACS Nano*, 9(2):1012–1057, 2015.

168 Qinghua Zhao, Guillaume Gouget, Jiaen Guo, Shengsong Yang, Tianshuo Zhao, Daniel B. Straus, Chengyuan Qian, Nuri Oh, Han Wang, Christopher B. Murray, and Cherie R. Kagan. Enhanced Carrier Transport in Strongly Coupled, Epitaxially Fused CdSe Nanocrystal Solids. *Nano Letters*, 21:3318–3324, 2021.

169 Yi-Hyuk Choi, Han Wang, Soong Ju Oh, Taejong Paik, Pil Sung Jo, Jinwoo Sung, Xingchen Ye, Tianshuo Zhao, Benjamin T. Diroll, Christopher B. Murray, and Cherie R. Kagan. Exploiting the colloidal nanocrystal library to construct electronic devices. *Science*, 352:205–208, 2016.

170 Cherie R. Kagan. Flexible colloidal nanocrystal electronics. *Chemical Society Reviews*, 48:1626–1641, 2019.

171 Cherie R. Kagan, Tai-hwan Hyeon, Dae-Hyeong Kim, Ricardo Ruiz, Maryann C. Tung, and H.-S. Philip Wong. Self-assembly for electronics. *MRS Bulletin*, 45:807–814, 2020.

172 Mengxia Liu, Nuri Yazdani, Maksym Yarema, Maximilian Jansen, Vanessa Wood, and Edward H. Sargent. Colloidal quantum dot electronics. *Nature Electronics*, 4:548–558, 2021.

173 Dmitri V. Talapin, Jong-Soo Lee, Maksym V. Kovalenko, and Elena V. Shevchenko. Prospects of Colloidal Nanocrystals for Electronic and Optoelectronic Applications. *Chemical Reviews*, 110:389–458, 2010.

174 Cherie R. Kagan, Lee C. Bassett, Christopher B. Murray, and Sarah M. Thompson. Colloidal Quantum Dots as Platforms for Quantum Information Science. *Chemical Reviews*, 121:3186–3233, 2021.

175 Auguste M. Urbas, Zubin Jacob, Luca Dal Negro, Nader Engheta, A. D. Boardman, P. Egan, Alexander B. Khpaniko, Vinod Menon, Marcello Ferrera, Nathaniel Kinsey, Clayton DeVaulet, Jongbum Kim, Vladimir Shalasev, Jason Valentine, Carl Pfeiffer, Anthony Grbic, Evgenii Narimianov, Linxiao Zhou, Shanxin Fan, Andrea Alù, Ekaterina Poutrina, Natalia M. Litchinitser, Mikhail A. Noginov, Kevin F. MacDonald, Eric Plum, Xiaoying Liu, Paul F. Nealey, Cherie R. Kagan, Christopher B. Murray, Durata A. Pawlak, Igor F. Smolyaninov, Vera N. Smolyaninova, and Debashis Chanda. Roadmap on optical metamaterials. *Journal of Optics*, 18:093005, 2016.

176 Taejong Paik, Hongseok Yun, Biaise Fleury, Sung-Hoon Hong, Pil Sung Jo, Yaoting Wu, Soong-Ju Oh, Matteo Cargnello, Haoran Yang, Christopher B. Murray, and Cherie R. Kagan. Hierarchical Materials Design by Pattern Transfer Printing of Self-Assembled Binary Nanocrystal Superlattices. *Nano Letters*, 17:1387–1394, 2017.

177 Jiaen Guo, Ji-Young Kim, Mingliang Zhang, Haonan Wang, Aaron Stein, Christopher B. Murray, Nicholas A. Kotov, and Cherie R. Kagan. Chemo- and Thermomechanically Configurable 3D Optical Metamaterials Constructed from Colloidal Nanocrystal Assemblies. *ACS Nano*, 14:1427–1435, 2020.

178 Sunkyu Yu, Cheng-Wei Qu, Yidong Chong, Salvatore Torquato, and Namkoo Park. Engineered disorder in photonics. *Nature Reviews Materials*, 6:226–243, 2021.

179 Ivan I. Smalyukh. Liquid Crystal Colloids. *Annual Review of Condensed Matter Physics*, 9:207–226, 2018.

180 Young-Ki Kim, JungHyun Noh, Karthik Nayani, and Nicholas L. Abbott. Soft matter from liquid crystals. *Soft Matter*, 15:6913–6929, 2019.

181 Zachary M. Sherman, Michael P. Howard, Beth A. Lindquist, Ryan B. Jadrich, and Thomas M. Truskett. Inverse methods for design of soft materials. *The Journal of Chemical Physics*, 152:140902, 2020.

182 Andrew W. Long and Andrew L. Ferguson. Rational design of patchy colloids via landscape engineering. *Molecular Systems Design & Engineering*, 3:49–65, 2018.

183 Duyu Chen, G. Zhang, and Salvatore Torquato. Inverse Design of Colloidal Crystals via Optimized Patchy Interactions. *The Journal of Physical Chemistry B*, 122:8462–8468, 2018.

184 Yutao Ma and Andrew L. Ferguson. Inverse design of self-assembling colloidal crystals with omnidirectional photonic bandgaps. *Soft Matter*, 15:8808–8826, 2019.

185 Greg van Anders, Daphne Kloots, Andrew S. Karas, Paul M. Dodd, and Sharon C. Glotzer. Digital Alchemy for Materials Design: Colloids and Beyond. *ACS Nano*, 9(10):9542–9553, 2015.

186 Yina Geng, Greg van Anders, Paul M. Dodd, Julia Dshemuchadse, and Sharon C. Glotzer. Engineering entropy for the inverse design of colloidal crystals from hard shapes. *Science Advances*, 5(7):eaaw0514, 2019.

187 Salvatore Torquato. Inverse optimization techniques for targeted self-assembly. *Soft Matter*, 5:1157–1173, 2009.

188 Carl S. Adorf, James Antonaglia, Julia Dshemuchadse, and Sharon C. Glotzer. Engineering entropy for the self-assembly of complex structures. *The Journal of Chemical Physics*, 149(20):204102, 2018.

189 Matthew Spellings, Julia Dshemuchadse, and Sharon C. Glotzer. Autonomous Exploration of Self-Assembly Simulation Parameter Space Using Machine Learning. *in preparation*, 2021.

190 Chengyu Dai and Sharon C. Glotzer. Efficient Phase Diagram Parameter Space Using Machine Learning. *Soft Matter*, 15:8808–8826, 2019.

191 Wesley F. Reinhart and Athanassios Z. Panagiotopoulos. Auto-
mated crystal characterization with a fast neighborhood graph analysis method. Soft Matter, 14:6083–6089, 2018.

192Heiner Friedrich, Cedric J. Gommes, Karin Overgaag, Johannes D. Meeldijk, Wiel H. Evers, Bart de Nijs, Mark P. Boneschanscher, Petra E. de Jongh, Arie J. Verkleij, Krijn P. de Jong, Alfons van Blaaderen, and Daniel Vanmaekelbergh. Quantitative Structural Analysis of Binary Nanocrystal Superlattices by Electron Tomography. Nano Letters, 9(7):2719–2724, 2009.

193Jun Chen, Xingchen Ye, and Christopher B. Murray. Systematic Electron Crystallographic Studies of Self-Assembled Binary Nanocrystal Superlattices. ACS Nano, 9(7):2719–2724, 2010.

194Jungwon Park, Haipei Zheng, Won Chul Lee, Phillip L. Geissler, Eran Rabani, and A. Paul Alivisatos. Direct Observation of Nanoparticle Superlattice Formation by Using Liquid Cell Transmission Electron Microscopy. ACS Nano, 6(3):2078–2085, 2012.

195Ingmar Swart, Peter Liljeroth, and Daniel Vanmaekelbergh. Scanning probe microscopy and spectroscopy of colloidal semiconductor nanocrystals and assembled structures. Chemical Reviews, 116:11181–11219, 2016.

196Kaifu Bian, Joshua J. Choi, Ananth Kaushik, Paulette Clancy, Detlef-M. Smilgies, and Tobias Hamnath. Shape-Anisotropy Driven Symmetry Transformations in Nanocrystal Superlattice Polymorphs. ACS Nano, 5(4):2815–2823, 2011.

197Kevin G. Yager, Yugang Zhang, Fang Lu, and Oleg Gang. Periodic lattices of arbitrary nano-objects: modeling and applications for self-assembled systems. Journal of Applied Crystallography, 47:118–129, 2014.

198Andrew Senesi and Byoungdu Lee. Scattering functions of polyhedra. Journal of Applied Crystallography, 48:565–577, 2015.

199Tao Li, Andrew J. Senesi, and Byoungdu Lee. Small Angle X-ray Scattering for Nanoparticle Research. Chemical Reviews, 116:11128–11180, 2016.

200Detlef-M. Smilgies. GIXAS: A versatile tool to assess structure and self-assembly kinetics in block copolymer thin films. Journal of Polymer Science, early view, 2021.

201Mark C. Weidman, Detlef-M. Smilgies, and William A. Tisdale. Kinetics of the self-assembly of nanocrystal superlattices measured by real-time in situ X-ray scattering. Nature Materials, 15:775–782, 2016.

202Yuzi Liu, Xiao-Min Lin, Yugang Sun, and Tijana Rajh. In Situ Visualization of Self-Assembly of Charged Gold Nanoparticles. Journal of the American Chemical Society, 135:3764–3767, 2013.

203Eli Sutter, Peter Sutter, Alexei V. Tkachenko, Roman Krahne, Joost de Graaf, Milena Arciniegas, and Liberato Manna. In situ microscopy of the self-assembly of branched nanocrystals in solution. Nature Communications, 7:11213, 2016.

204Kyungtae Kim, Morgan W. Schulze, Akash Arora, Ronald M. Lewis, Marc A. Hillmyer, Kevin D. Dorfman, and Frank S. Bates. Thermal processing of diblock copolymer melts mimics metallurgy. Science, 356:520–523, 2017.

205Neven Caplar, Sandro Tacchella, and Simon Birrer. Quantitative evaluation of gender bias in astronomical publications from citation counts. Nature Astronomy, 1(6):0141, 2017.

206Jordan D. Dworkin, Kristina A. Linn, Erin G. Teich, Perry Zurn, Russell T. Shinohara, and Danielle S. Bassett. The extent and drivers of gender imbalance in neuroscience reference lists. Nature Neuroscience, 2020.

207Paula Chatterjee and Rachel M Werner. Gender disparity in citations in high-impact journal articles. JAMA Netw Open, 4(7):e2114509, 2021.

208Jordan Dworkin, Perry Zurn, and Danielle S. Bassett. (In)citing Action to Realize an Equitable Future. Neuron, 106(6):890–894, 2020.

209Dale Zhou, Eli J. Cornblath, Jennifer Stiso, Erin G. Teich, Jordan D. Dworkin, Ann S. Blevins, and Danielle S. Bassett. Gender Diversity Statement and Code Notebook v1.0. Zenodo, February 2020.