

Final Report

for

Grant # DE-FG02-02ER46000

Simulations of Self-Assembly of Tethered Nanoparticle Shape Amphiphiles.

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1 PROJECT GOALS

Self-assembly of nanoparticle building blocks including nanospheres, nanorods, nanocubes, nanoplates, nanoprisms, etc., may provide a promising means for manipulating these building blocks into functional and useful materials. One increasingly popular method for self-assembly involves functionalizing nanoparticles and nanostructured molecules with “tethers” of organic polymers or biomolecules with specific or nonspecific interactions to facilitate their assembly. However, there is little theory and little understanding of the general principles underlying self-assembly in these complex materials. Using computer simulation to elucidate the principles of self-assembly and develop a predictive theoretical framework was the central goal of this project.

In the project periods prior to this one, we proposed the general conceptual framework for patchy particles and polymer-tethered nanoparticles (TNP). Under this grant, we developed computational tools for the study of self-assembly of TNP systems and applied those tools to the design and reverse engineering of new TNP building blocks capable of self-assembling into novel structures with desired functionalities. We predicted the existence of a number of novel phases and of new avenues for reconfigurable materials. We developed new simulation and analysis techniques to carry out these investigations, and we made these technologies available to the broader DOE research community. We extended the paradigm of patchy particles to include entropically patchy particles - particles for which the “patches” are entropic - and proposed a conceptual framework for assembling materials based on particle shape. We also investigated ways of storing information with colloidal matter and proposed the idea of “digital colloids”.

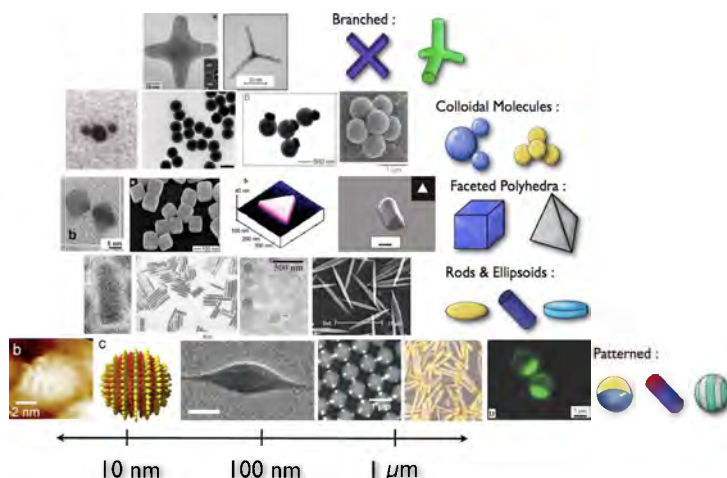


Fig. 1. Examples of nano and colloidal building blocks reported in the literature. See article for original image references. From S.C. Glotzer and M.J. Solomon, *Nature Materials*, 2007. Supported by DE-FG02-02ER46000.

The materials of the future will not be actively assembled through careful placement of nano-scale precursors, but, rather, self-assembled through a careful and deliberate choice of specifically designed particles with a predisposition to arrange into a desired target structure under favorable conditions. This process of “self-assembly” is ubiquitous in nature, dominating even the basic processes that occur inside cells, and serves as in inspiration for the design of next-generation materials. These materials will possess on-demand functionality, have hierarchical and complex assembly behavior, and even be able to reconfigure based upon active or ambient conditions present in the system. Our investigations of TNPs predicted and explained numerous previously unidentified phases and helped to further expand our set of design rules for creating self-assembled structures with “on-demand” functionality. We also drove the exploration of the role of shape in the nanoparticle design space. Toward this end, we developed models for representing shape in two and three spatial dimensions for Molecular Dynamics (MD) as well as finite packings and reconfigurability on demand.

2 SUMMARY OF ACCOMPLISHMENTS DURING PERIOD OF GRANT (2009-2013)

2.1. Workforce development

Six PhD students – Carolyn Phillips, Trung Dac Nguyen, Ryan Marson, Jaime Millan, Samanthule Nola, and Wenbo Shen - and postdocs Greg van Anders, Michael Engel and Jiang Hao were partially supported by this grant. Phillips held a DOE Computational Science Graduate Fellowship from 2006-2010, and in 2011 was selected as the Frederick A. Howes Scholar from all the CSGF recipients graduating that year. She was also selected to attend the prestigious Lindau Conference of Nobel Laureates. She completed her PhD in Applied Physics in 2011 (thesis: *Role of heterogeneity in self-assembled tethered and anisotropic nanoparticles*), was named to the prestigious Aneesur Rahman Postdoctoral Fellowship at Argonne National Laboratory, awarded internationally on an annual basis to an outstanding doctoral scientist or engineer in the early stages of a promising career, and recently was hired a permanent member of the research staff at Argonne. Nguyen completed his PhD in Chemical Engineering (thesis: *Computer-aided design of nanostructures from self- and directed-assembly of soft matter building blocks*) in 2011 and is now a postdoctoral fellow at Oak Ridge National Laboratory. Marson, Millan, Nola and Shen are nearing completion of their doctoral work and each anticipates a thesis defense in late 2014 or 2015. Engel and van Anders are now Research Investigators at the University of Michigan, and Jiang is a Programmer Analyst at Tessella, Inc., in Houston TX. Two undergraduate students, Michelle Marval and Jeremy Kapala, also were supported (summer 2011) and contributed to the research; Marval was a co-author on Phys. Rev. E (2012).

2.2. Output and recognition

During the project period, our work resulted in 23 publications (including papers in PRL, PRE, PNAS, JCP, ACS Nano, and Nano Letters), 44 contributed talks or posters by students and postdocs, and 89 invited talks by the PI at national and international conferences, workshops, and departmental colloquia, including eight named lectureships. The seminal Progress article in Nature Materials (2007) by Glotzer and Solomon which, in the reporting period prior to this one, introduced our conceptual framework for building block anisotropy for self-assembly has been cited 905 times as of this writing and in 2012 it was named one of the top 20 landmark articles in Nature Materials from 2002-2012, the first 10 years of that journal. Two Physical Review publications in 2012 received publicity from the American Physical Society and popular press including Science Daily, U-M News Service, AoNano.com and dozens of “technology watch” websites. Additional publicity links on our work may be found on our website <http://www.engin.umich.edu/dept/che/research/glotzer/>. During this project period and based in part on research conducted under this grant, the PI was elected a member of the American Academy of Arts and Sciences and named a Simons Investigator, the Stuart W. Churchill Collegiate Professor of Chemical

Engineering at the University of Michigan, and a DoD National Security Science and Engineering Faculty Fellow. In 2014, the PI was elected a Fellow of American Association for the Advancement of Science and elected to the National Academy of Sciences.

2.3. Unexpended funds

No unexpended funds remained at end of the grant period. The HPC nodes remain integrated into the cluster and will continue to be used for further research until they are retired in 2015. All work was conducted at the University of Michigan.

3 DETAILED ACCOMPLISHMENTS DURING PERIOD OF GRANT (2009-2013)

Since this project was last renewed at the end of 2008, we investigated a diverse range of tethered nanoparticle and related systems. As elaborated briefly in the sections below, we discovered a dodecagonal quasicrystal phase in a system of tethered nanospheres and, based on our findings, proposed a simple model that explains the formation of all soft matter (micellar) quasicrystals (published in PNAS); motivated by experiments we showed that slight amounts of polydispersity in the size of the nanoparticle can stabilize the elusive gyroid phase (published in Soft Matter); we showed how networks of self-assembled tethered nanorods can reconfigure from one to another upon change in rod length faster than they can assemble from a disordered phase (published in ACS Nano); we showed that ligands adsorbed on the surface of a nanoparticle will naturally migrate to the corners and edges, rather than the faces, of the nanoparticle due to entropic effects, which can produce patchy NP-NP interactions (published in Nanoscale); and we investigated a new class of telechelic nanoparticles and discovered a host of new complex self-assembled phases (published in Nano Letters). We also developed several important new computational tools necessary for the simulation of nanoparticles and which can be applied to a wide class of systems. We developed shape matching codes for analyzing structures via their local motifs and comparing them against known reference structures (published as an invited contribution to Annual Reviews of Condensed Matter Physics and in J. Computational Physics). We wrote new algorithms to simulate rigid bodies and dissipative particle dynamics interactions on graphics processors (published in Computer Physics Communications and the Journal of Computational Physics, respectively). We invented a new algorithm – *filling* – as an efficient method for simulating anisometric nanoparticles as rigid collections of overlapping spheres of different sizes chosen to best represent the desired NP shape (published in PRL and Physics Procedia). We discovered that filling is in fact a new class of spatial subdivision problems, intermediate between packing and covering. We introduced the notion of entropically patchy particles as the entropic counterpart to enthalpically patchy particles and proposed a theoretical framework that defines and quantifies *directional entropic forces* and demonstrates the anisotropic—that is, patchy—nature of these emergent, attractive forces. Finally, we showed how reconfigurable clusters made of N colloidal particles bound flexibly to a central colloidal sphere have the capacity to store high densities of information. The model was validated experimentally with an $N=4$ reconfigurable cluster from chemically synthesized colloidal building blocks, which demonstrated state switching in agreement with simulations. This cluster can store one bit of information, and represents the simplest digital colloid. This work appeared recently on the cover of Soft Matter; at the time of this writing it has already received considerable press coverage. While each of these accomplishments broke new ground in their own right, collectively they contribute to a greater understanding, and predictive capability, of the self-assembly of anisotropically-interacting soft matter systems.

3.1 Complex structures from Tethered Nanoparticles

Long molecular ligands or "tethers" play an important role in the self-assembly of many nanoscale systems. These tethers, whose only interaction may be a hard-core repulsion, contribute significantly to the free energy of the system because of their large conformational entropy. We carried out a computational study of the self-assembly of amphiphilic ditethered nanospheres using molecular

simulation.^{1,2} As a function of the interaction strength and directionality of the tether-tether interactions, we predicted the formation of four highly ordered phases not previously reported for nanoparticle systems. We found a double diamond structure composed of a zinc blende (binary diamond) arrangement of spherical micelles with a complementary diamond network of nanoparticles (ZnS/D), a phase of alternating spherical micelles in a NaCl structure with a complementary simple cubic network of nanoparticles to form an overall crystal structure identical to that of AlCu(2)Mn (NaCl/SC), an alternating tetragonal ordered cylinder phase with a tetragonal mesh of nanoparticles described by the [8,8,4] Archimedean tiling (TC/T), and an alternating diamond phase in which both diamond networks are formed by the tethers (AD) within a nanoparticle matrix (see Figure 2). We compared these structures with those observed in linear and star triblock copolymer systems. Additionally, we reported the results of a computational study of the self-assembly of amphiphilic ditethered nanospheres using molecular simulation. We explored the phase behavior as a function of nanosphere diameter, interaction strength, and directionality of the tether-tether interactions. We predicted the formation of seven distinct ordered phases and compared these structures with those observed in linear and star triblock copolymer systems.

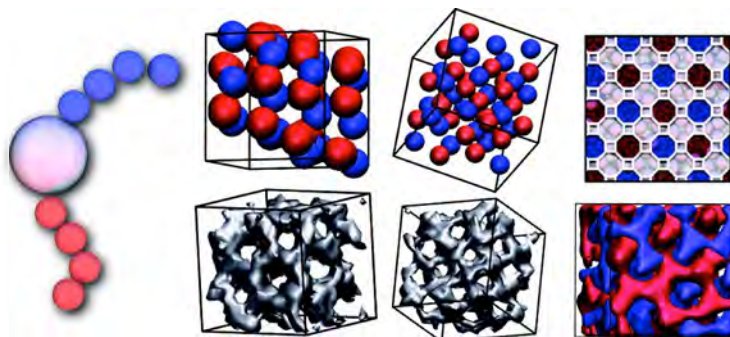


Figure 2. Schematic of the ditethered nanosphere, and the resulting highly ordered phases predicted by molecular simulations.

One-dimensional nanostructures such as cylinders and tubules are of great interest owing to their unique electro-optical properties and potential applications in areas ranging from nanotechnology to biotechnology, but they are challenging to synthesize. In 2009 we reported the formation of the first hollow tubules to spontaneously form scrolls from the self-assembly of T-shaped rod-coil molecules in the solid state.³ Our predictions were subsequently validated by experiments.

We investigated how simple approximate models can be developed and used to quickly determine the configurations into which tethers will self assemble in nanoscale systems and derived criteria that determine when these models are expected to be accurate.⁴ We proposed a generalized two-body approximation that can be used as a toy model for the self-assembly of tethers in systems of arbitrary geometry, applied this to the self-assembly of self-assembled monolayers on a planar surface, and compared our results to those in the literature obtained via atomistic and dissipative particle dynamics simulations.



Figure 3. Zig-zag lamellae formed by end-tethered nanorods.

We reported a computational study of the self-assembly of end-tethered nanorods in a neat system (no solvent).⁵ We presented morphological phase diagrams for low and moderate aspect ratio rods as a function of inverse temperature vs. relative tether fraction. Our simulations predicted that the end-tethered rods self-assemble into hexagonally arranged chiral cylinders, hexagonally perforated lamellae, monolayer and bilayer arrowhead structures and wavy lamellae (see Figure 3). For high aspect ratio tethered nanorods and small tether fractions, we observed that the tethered nanorods self-assemble into smectic and zig-zag lamellar morphologies.

Motivated by growing interest in the self-assembly of nanoparticles for applications such as photonics, organic photovoltaics, and DNA-assisted designer crystals, we explored the phase behavior of tethered spherical nanoparticles.⁶ We used a polymer tether to geometrically constrain a pair of nanoparticles, creating a tethered nanoparticle “telechelic”. Using simulation, we examined how varying architectural features, such as the size ratio of the two end-group nanospheres and the length of the flexible tether, affect self-assembled morphologies. We demonstrated not only that this hybrid building block maintains the same phase diversity as linear triblock copolymers, allowing for a variety of nanoparticle materials to replace polymer blocks, but also that new structures not previously reported are accessible (see Figure 4). Our findings imply a robust underlying ordering mechanism is common among these systems, thus allowing flexibility in synthesis approaches to achieve target morphologies.

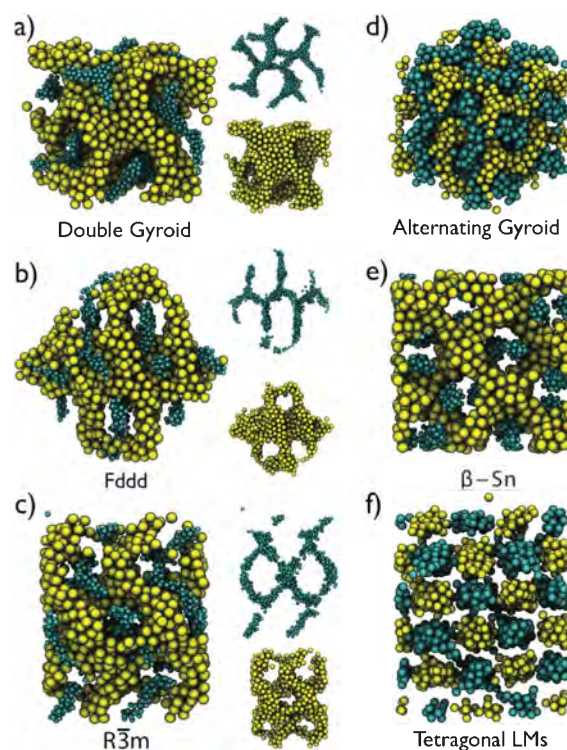


Figure 4. Tethered nanoparticle telechelics exhibit similar phase behavior to triblock copolymers, allowing a variety of these structures to be functionalized with nanoparticles.

Effect of Polydispersity on the Stability of the Gyroid

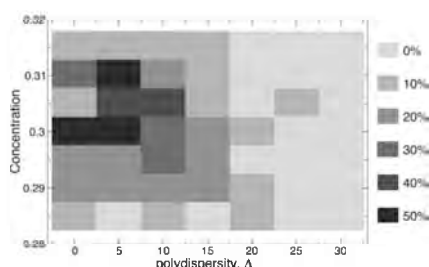


Figure 5. A survey of the TNS phase diagram for various packing fractions, with darkness indicating the probability of observing the DG.

Early simulations under prior reporting periods predicted that aggregating nanospheres functionalized with polymer “tethers” can self-assemble to form the double gyroid (DG) phase seen in block copolymer and surfactant systems.⁷ Within the struts of the gyroid, the nanoparticles pack in icosahedral motifs, stabilizing the gyroid phase in a small region of the phase diagram. We studied the impact of nanoparticle size polydispersity on the stability of the double gyroid phase.⁸ We showed for low amounts of polydispersity the energy of the double gyroid phase is lowered. A large amount of polydispersity raises the energy of the system, disrupts the icosahedral packing, and eventually destabilizes the gyroid. Our results showed that the DG forms readily up to 10% polydispersity. Considering polydispersity as high as 30%, our results suggest no terminal polydispersity for the DG, but that higher polydispersities may kinetically inhibit phase formation. The inclusion of a small population of either smaller or larger nanospheres encourages low-energy icosahedral clusters and increases the gyroid stability while facilitating its formation. We also introduced a new measure for determining the volume of a component in a microphase-separated system based on the Voronoi tessellation (reference Phillips and Glotzer, preprint).

Using multiple thermodynamic paths to explore the phase diagram as a function of temperature and polydispersity, we further explored the effect of nanosphere size polydispersity on the phase diagram.⁹ We showed that in the portions of the phase diagram characterized by an icosahedral local nanoparticle

packing motif, a low amount of polydispersity lowers the energy and a large amount of polydispersity raises the energy of the system by disrupting the icosahedral packing. In general, regions of the phase diagram characterized by liquid-like icosahedral packing have high terminal polydispersities from 15% to more than 30%. In the regions of the phase diagram characterized by crystalline local packing, polydispersity raises the energy of the system and induces a phase transition from crystalline to liquid-like ordering within the nanosphere rich regions of the microphase. We found that the bilayer crystalline lamellae phase has a terminal polydispersity of 6%, but may still be partially crystalline up to 12%.

Effect of Reconfigurability on self assembly of tethered nanorods

Reconfigurable nanostructures represent an exciting new direction for materials. Applications of reversible transformations between nanostructures induced by molecular conformations under external fields can be found in a broad range of advanced technologies including smart materials, electromagnetic sensors, and drug delivery. Shape-changing nanoparticles provide a conceptually new and exciting approach to self-assembly and phase transformations by providing tunable parameters fundamentally different from the usual thermodynamic parameters. We investigated, via molecular simulation, a transformation between two thermodynamically stable structures self-assembled by laterally tethered nanorods whose rod length is switched between two values.¹⁰ Building blocks with longer rods assembled into a square grid structure, while those with short rods formed bilayer sheets with internal smectic A ordering at the same thermodynamic conditions. By shortening or lengthening the rods over a short time scale relative to the system equilibration time, we observed a transformation from the square grid structure into bilayer sheets, and vice versa. We also observed honeycomb grid and pentagonal grid structures for intermediate rod lengths. The reconfiguration between morphologically distinct nanostructures induced by dynamically switching the building block shape motivates the fabrication of shape-changing nanoscale building blocks as a new approach to the self-assembly of reconfigurable materials. This work was an ACS Nano cover article in 2012 (see Figure 6).



Figure 6. Example phases of reconfigurable tethered nanorods.

Soft Matter Quasicrystals

Through simulations of mono- and di-tethered nanoparticles, we explained entropically stabilized quasicrystals in soft matter systems. Specifically, we used molecular simulation to demonstrate an alternative approach for assembling dodecagonal quasicrystals and their approximants based solely on particle functionalization and shape.¹¹ These effects mimic the characteristics of the specialized potentials, thereby replacing complex energetic interactions with simpler-to-achieve bonded and excluded-volume interactions. Our model consists of spherical building blocks functionalized with mobile surface entities to encourage the formation of structures with low surface contact area, including non-close-packed and polytetrahedral structures. The building blocks also possess shape polydispersity, where a subset of the building blocks deviates from the ideal spherical shape, which discourages the formation of close-packed crystals. We showed that a model system possessing both mobile surface entities and shape polydispersity consistently assembles complex quasicrystal-like structures (See Figure 7). We also reported the spontaneous assembly of approximants in two micelle-forming systems of tethered nanoparticle building blocks that possess these key features. We argued that this mechanism can be widely exploited to assemble quasicrystals and approximants on the nano and microscale, and may further elucidate the recent formation of soft matter quasicrystals in experiment. In a broader sense, our

study demonstrated how complex interaction potentials can be replicated by packing analogues, and serves as a model for future applications involving unique structures.

3.2 Methodological Developments – DPD and Rigid Bodies

Two manuscripts benchmarking and describing our GPU-based, open source molecular dynamics code, HOOMD-Blue, were published during the reporting period and are partially supported by this grant.

Brownian Dynamics (BD), also known as Langevin Dynamics, and Dissipative Particle Dynamics (DPD) are implicit solvent methods commonly used in models of soft matter and biomolecular systems. We developed a new method in which a micro-stream of pseudorandom numbers is generated in each thread and kernel call.¹² These high quality, statistically robust micro-streams require no global memory for state storage, are more computationally efficient than other schemes in memory-bound kernels, and uniquely enable the DPD simulation method without requiring communication between threads. The scheme is 2-7 times faster than previous schemes for the DPD thermostat. To our knowledge, HOOMD-blue is the only GPU MD code package that can perform Dissipative Particle Dynamics simulations.

We extended the basic Molecular dynamics methods in HOOMD-Blue to include rigid body constraints so as to enable composite particles with complex shapes such as anisotropic nanoparticles, grains, molecules, and rigid proteins to be modeled.¹³ HOOMD-Blue can now simulate systems of particles, rigid bodies, or mixed systems in microcanonical (NVE), canonical (NVT), and isothermal-isobaric (NPT) ensembles. In typical cases, HOOMD-blue on a single GTX 480 executes 2.5-3.6 times faster than LAMMPS executing the same simulation on any number of CPU cores in parallel. Simulations with rigid bodies may now be run with larger systems and for longer time scales on a single workstation than was previously even possible on large clusters.

Filling Solutions

Covering and packing problems have long been studied and are very well understood. The packing problem asks how to pack N objects inside a given shape such that no two objects overlap. The covering problem asks how to place N overlapping objects over a shape so that the entire area of the shape is covered. We asked a related question “Given a computer simulation capable of modeling anisotropic nanoparticles with only N balls, what is the best way to represent arbitrary shapes?”¹⁴ A packing of N identical balls tied together to move as a rigid body is a reasonable solution, but obtaining an accurate representation necessitates high N , which slows the simulation. A better solution is to *fill* the shape with N polydisperse, overlapping balls as shown at right. Formally, we define the *filling* problem as a question of how to place N polydisperse balls each contained entirely inside a shape G so as to maximally cover the area of G . We

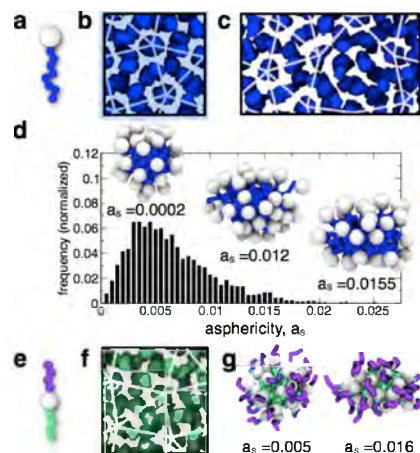


Figure 7. Quasicrystalline assemblies from TNPs. (a) Building block. (b)-(c) QC assemblies. (d) Micelle asphericity. (e) di-TNP building block. (f) QC assembly. (g) Micelle asphericity.

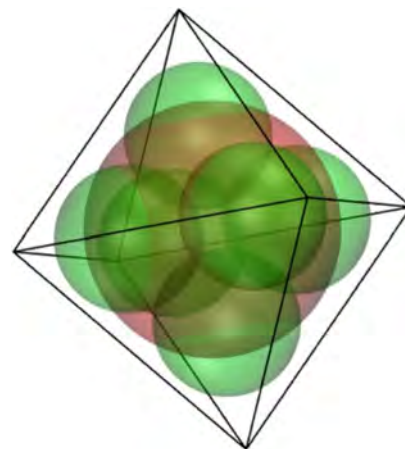


Figure 8. Filling solution for an octahedron.

examined this problem analytically first, and prove that there exists an optimal covering solution consisting only of *maximal* balls (balls that touch the surface of G at two or more points), and compute the density of balls as N goes to infinity for simple polygons. The filling problem is a global optimization problem with a complex solution space. So analytical solutions for arbitrary N , such as those desired for use in the aforementioned simulations, are not tractable. Instead, we used numerical nonlinear optimization techniques and develop computer codes that find an approximate optimal filling given any simple polygon and any N . Extensive classification of the behavior of the solutions led us to several conjectures about the behavior of the solution space. These conjectures enable smart heuristics to be programmed into the codes that decrease the time spent searching for optimal solutions while at the same time increasing their accuracy and precision. We further extended our codes to find optimal fillings for polyhedra,¹⁵ creating highly coarse-grained representations of complex particles by rigidly connecting beads into a composite particle. We showed that by permitting the beads to vary in radii and to overlap, particles can be modeled with more complicated shapes, approaching perfect polygons and polyhedra in two and three dimensions, respectively. The positions and radii of the beads correspond to a *filling* solution of the very short-range repulsive shape of the modeled nanoparticle.

Shape Matching

Many standard structural characterization quantities, such as order parameters and correlation functions, exist for common condensed matter systems, such as spherical and rod-like particles. However, these structural quantities are often insufficient for characterizing the unique and highly complex structures often encountered in the emerging field of nano and microscale self-assembly, or other disciplines involving complex structures such as computational biology. Computer science algorithms known as "shape matching" methods pose a unique solution to this problem by providing robust metrics for quantifying the similarity between pairs of arbitrarily complex structures. This pairwise matching operation, either implicitly or explicitly, lies at the heart of most standard structural characterization schemes for particle systems. By substituting more robust "shape descriptors" into these schemes we extended their applicability to structures formed from more complex building blocks (see Figure 9). We described several structural characterization schemes and shape descriptors that can be used to obtain various types of structural

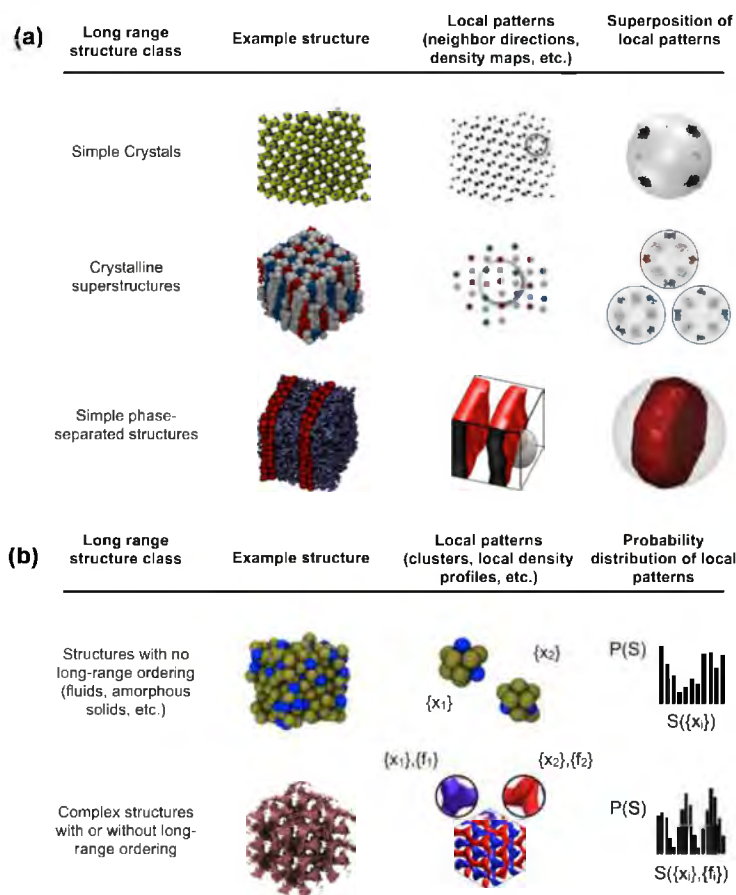


Figure 9. Depiction of strategies for extracting global patterns. (a) Global patterns by superposition – for structures with long range orientational ordering, a global pattern can be extracted by translating all local clusters or density maps to a common origin. (b) For structures with no long range orientational ordering or complex structures with many important directions, a global pattern can be built up from the probability distribution of local patterns.

information about particle systems.^{16,17} We demonstrated the application of shape matching algorithms to a variety of example problems, for topics including local and global structure identification and classification, automated phase diagram mapping, and the construction of spatial and temporal correlation functions. The methods are applicable to a wide range of systems, both simulated and experimental, provided particle positions are known or can be accurately imaged.

3.3 Patchy Particles

Patch formation by ligands on faceted nanoparticles

Long molecular ligands or "tethers" play an important role in the self-assembly of many nanoscale systems. These tethers, whose only interaction may be a hard-core repulsion, contribute significantly to the free energy of the system because of their large conformational entropy. We developed simple approximate models to quickly determine the configurations into which tethers will self assemble in nanoscale systems.¹⁸ We derived criteria that determine when these models are expected to be accurate. Finally, we proposed a generalized two-body approximation that can be used as a toy model for the self-assembly of tethers in systems of arbitrary geometry and applied this to the self-assembly of self-assembled monolayers on a planar surface. We compared our results to those in the literature obtained via atomistic and dissipative particle dynamics simulations.

Entropically Patchy Particles

Patchy particles are a popular paradigm for the design and synthesis of nanoparticles and colloids for self-assembly. In "traditional" patchy particles, anisotropic interactions arising from patterned coatings, functionalized molecules, DNA, and other enthalpic means, create the possibility for directional binding of particles into higher-ordered structures. Although the anisotropic geometry of nonspherical particles contributes to the interaction patchiness through van der Waals, electrostatic, and other interactions, how particle shape contributes entropically to self-assembly is only now beginning to be understood. The directional nature of entropic forces has recently been elucidated. A recently proposed theoretical framework that defines and quantifies directional entropic forces demonstrates the anisotropic – that is, patchy – nature of these emergent, attractive forces.¹⁹ We introduced the notion of entropically patchy particles as the entropic counterpart to enthalpically patchy particles. Using three example "families" of shapes, we showed how to modify entropic patchiness by introducing geometric features to the particles *via* shape operations so as to target specific crystal structures assembled here with Monte Carlo simulations. We quantified the emergent entropic valence *via* a potential of mean force and torque. We showed that these forces are on the order of a few $k_B T$ at intermediate densities below the onset of crystallization. We generalized these shape operations to shape anisotropy dimensions, in analogy with the anisotropy dimensions introduced for enthalpically patchy particles. Our findings demonstrate that entropic patchiness and emergent valence provide a way of engineering directional bonding into nanoparticle systems, whether in the presence or absence of additional, non-entropic forces.

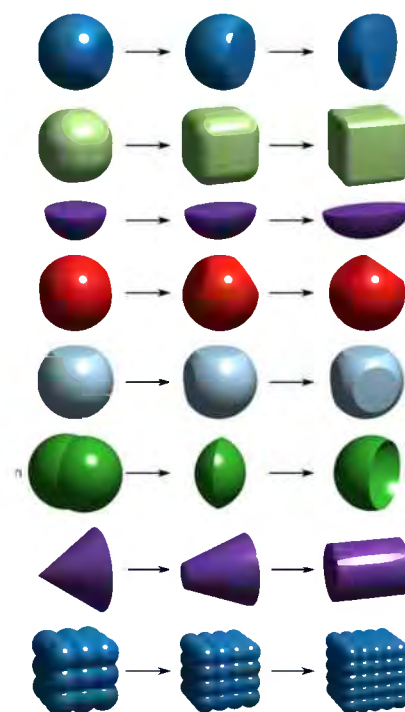


Figure 10. Anisotropy dimensions for entropically patchy particles control local packing and thus assembly.

Packing and Shape

Packings of hard polyhedra have been studied for centuries due to their mathematical aesthetic and more recently for their applications in fields such as nanoscience, granular and colloidal matter, and biology. In all these fields, particle shape is important for structure and properties, especially upon crowding. We explored packing as a function of shape. By combining simulations and analytic calculations, we studied three two-parameter families of hard polyhedra and report an extensive and systematic analysis of the densest known packings of more than 55,000 convex shapes.²⁰ The three families have the symmetries of triangle groups (icosahedral, octahedral, tetrahedral) and interpolate between various symmetric solids (Platonic, Archimedean, Catalan). We found optimal (maximum) packing-density surfaces that reveal unexpected richness and complexity, containing as many as 132 different structures within a single family. Our results demonstrate the importance of thinking about shape not as a static property of an object, in the context of packings, but rather as but one point in a higher-dimensional shape space whose neighbors in that space may have identical or markedly different packings. We presented and interpreted our packing results in a consistent and generally applicable way by proposing a method to distinguish regions of packings and classify types of transitions between them. This work was featured online by APS, Physics World, and New Scientist, among others.

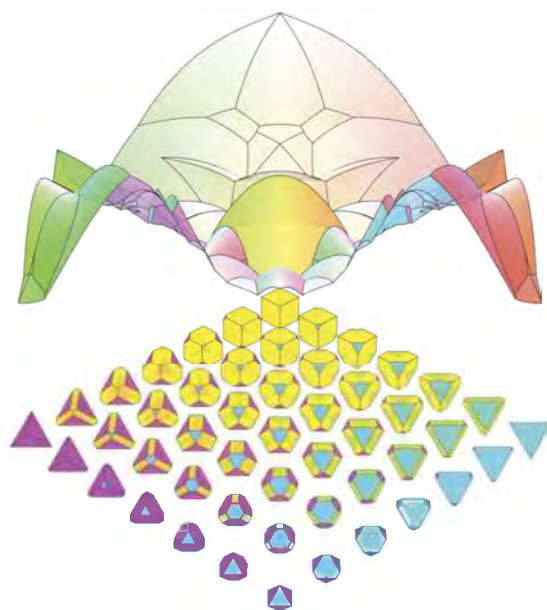


Figure 11. Optimal packing-density surface for polyhedra as a function of shape deformation.

Motivated by breakthroughs in the synthesis of faceted nano- and colloidal particles, as well as theoretical and computational studies of their packings, we investigated a family of truncated triangular bipyramids.²¹ We report dense periodic packings with small unit cells that were obtained via numerical and analytical optimization. The maximal packing fraction ϕ_{\max} changes continuously with the truncation parameter t . Eight distinct packings are identified based on discontinuities in the first and second derivatives of $\phi_{\max}(t)$. These packings differ in the number of particles in the fundamental domain (unit cell) and the type of contacts between the particles. In particular, we reported two packings with four particles in the unit cell for which both $\phi_{\max}(t)$ and $\phi'_{\max}(t)$ are continuous and the discontinuity occurs in the second derivative only. In the self-assembly simulations that we perform for larger boxes with 2048 particles, only one out of eight packings is found to assemble. In addition, the degenerate quasicrystal reported previously for triangular bipyramids without truncation assembles for truncations as high as 0.45. The self-assembly propensities for the structures formed in the thermodynamic limit are explained using the isoperimetric quotient of the particles and the coordination number in the disordered fluid and in the assembled structure.

Spherical Codes and Digital Colloids

Particles with attractive patches, also known as “patchy particles,” are of great interest in self-assembly because the anisotropy of precisely placed patches can be exploited to drive systems of patchy particles to self-assemble into complex and useful structures. Placing interaction patches on the surface of a sphere,

however, is experimentally challenging. We demonstrated a strategy to self-assemble the precise placement of four through twelve circular patches of DNA onto the surface of a spherical particle.²² These arrangements are unique, given a number of patches, and correspond to solutions of a well-studied mathematical optimization problem. Using complementary strands of DNA grafted onto the surfaces of “central” and “halo” particles we demonstrated the binding of halo particles onto central particles in Brownian dynamics simulations accelerated with general purpose graphics processors. These halo particles equilibrate on the surface of the central particle, and we show that free energy minimization via entropy maximization guides their arrangement. We performed free energy calculations predicting the arrangements of particles observed in simulation and explain counterintuitive arrangements.

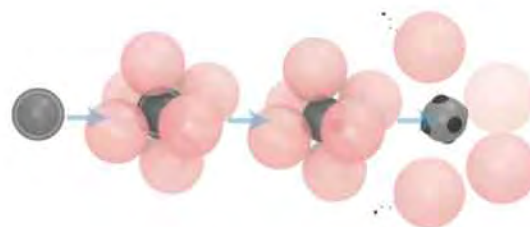


Figure 12. Our simulations predict the thermodynamically preferred arrangements of DNA-linked colloids adsorbed from a bath onto a central NP. In this design strategy, releasing of the unlinked DNA and then the “halo” particles would leave behind a patchy particle.

Through the design and manipulation of discrete, nanoscale systems capable of encoding massive amounts of information, the basic components of computation are open to reinvention. These components will enable tagging, memory storage, and sensing in unusual environments—elementary functions crucial for soft robotics and “wet computing.” Using Brownian dynamics simulations, we predicted dynamical regimes that allow for information to be written, saved, and erased.²³ We showed how reconfigurable clusters made of N colloidal particles bound flexibly to a central colloidal sphere have the capacity to store an amount of information that increases as $O(N \ln(N))$. An $N=4$ reconfigurable cluster was assembled experimentally by colleagues from chemically synthesized colloidal building blocks, and we monitored its equilibrium dynamics. We observed state switching in agreement with simulations. The cluster could store one bit of information, representing the simplest digital colloid. This work will appear on the cover of *Soft Matter*; at the time of this writing it is available online and has received considerable press coverage.

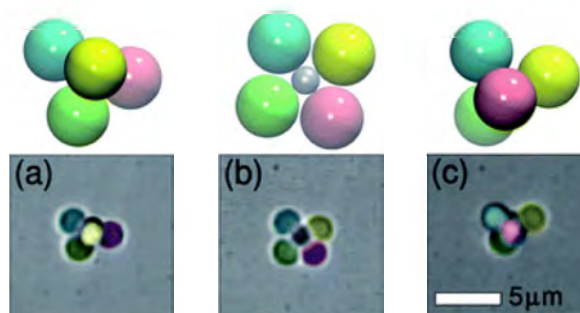


Figure 13. “Information states” of the 2-bit cluster and corresponding images from experiments.

PUBLICATIONS during reporting period 2009-2013

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