Mini-Review

ACCELERATED DISCOVERY OF NANOMATERIALS USING MOLECULAR SIMULATION

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Abstract. Next-generation nanotechnology demands new materials and devices that are highly efficient, multifunctional, cost-effective and environmentally friendly. The need to accelerate the discovery of new materials therefore becomes more pressing than ever. In this regard, among widely regarded fabrication techniques are self-assembly and directed assembly, which have attracted increasing interest as they are applicable to a wide range of materials ranging from liquid crystals to semiconductors to polymers and biomolecules. The fundamental challenges to these bottom up techniques are to design the assembling building blocks, to tailor their interactions and to engineering the assembly pathways towards desirable structures. We will demonstrate how molecular simulation, particularly Molecular Dynamics and Monte Carlo methods, has been a powerful tool for tackling these fundamental challenges. We will review through selected examples the insights from simulation that help explain the roles of the shape of the building blocks and their interactions in determining the morphology of the assembled structures. We will discuss testable predictions from simulation that serve to motivate future experimental studies. Aided by data mining techniques and computing capacities, the cooperative efforts between computational and experimental investigations open new horizons for accelerating the discovery of new materials and devices. We will address the theoretical background of self-assembly studies; simulation methods and data analysis tools commonly used in this highly multidisciplinary research area.

Keywords: materials design, self-assembly, computer simulation.

Classification numbers: 2.10.1; 2.4.4; 2.3.2

1. INTRODUCTION

The performance and quality of future technology are expected to be dictated at smaller length scales and shorter time scales. The search for new nanomaterials that have controllable properties and cost-effective has captured much interest in the past decade in a large part

because they would benefit a broad range of applications including, but not limited to, catalysis, electronics, energy conversion and storage, optical devices, and drug delivery. Much needed are fabrication methods that allow for precise control over the morphology of the underlying nanostructures and for ready for large-scale production. Towards this end, self- and directed-assembly techniques offer real opportunities to address such requirements. Self-assembly, a mechanism observed in most biological systems (e.g., protein folding and cell membrane formation), leads to the spontaneous organization of molecular and nanoscopic units, e.g., liquid crystals, polymers, nanoparticles and biomolecules, into thermodynamically stable structures. From the materials design perspectives, the fundamental challenges to these bottom up approaches include designing assembling building blocks, tuning their interactions and identifying possible routes toward target nanostructures.

The remarkable advances in synthetic techniques over the past decades allow for synthesis of assembling building blocks in almost arbitrary shapes, sizes and compositions. The building blocks may also be functionalized with short ligands, polymers and/or DNAs [1-11] to facilitate their assembly. In certain cases, these so-called colloidal molecules are able to respond to changes in temperature, ionic strength and electromagnetic frequencies in a similar fashion to actual molecules. Furthermore, the nature of the interactions between these building blocks is non-covalent, e.g., van der Waals forces, Coulombic forces, hydrogen bonding and hydrophobic/hydrophilic forces [12, 13], which are independent of chemical specificity. As a result, self- and directed-assembly at nanoscale is a problem well suited for molecular simulation studies, where coarse-grained models are often sufficient to represent the relevant interactions between the units.

Molecular simulation has been a powerful, and in many cases, indispensable, tool for investigating systems ranging from atomic to molecular to mesoscopic scales. Additionally, the past three decades have witnessed groundbreaking advances in electrical engineering, computer engineering and simulation algorithms. These accomplishments have made it possible to tackle problems on many orders of magnitude greater in time and length scales than earlier. Perhaps more interesting is the fact that nanomaterials design has become multidisciplinary, involving physics, chemistry, biology, mathematics, statistics and computer science. In this report, we aim to introduce a broad picture of computational studies on materials design via bottom up techniques and their roles in facilitating the discovery and design of new materials and devices. Given the rapid growth of these multidisciplinary research areas, it is inevitable that this report cannot be comprehensible. While we have attempted to discuss the work from pioneering research groups and influential studies in the field, the report is by no means comprehensive. Interested readers are encouraged to find excellent literature in Refs. [12-15].

The report is structured as follows. A short overview to the theoretical background, simulation methods and tools commonly used in self-assembly studies in Section 2. In Section 3, we will review several examples to demonstrate how simulation has helped explain the complex assembled structures and processes observed in experiment. In Section 4 we discuss the predictions provided by molecular simulation, which can be used as guidance to further experimental efforts. Finally, we envision the roles of molecular simulation in support of data mining techniques and computing capabilities accelerating the discovery of new nanomaterials.

2. THEORY, SIMULATION METHODS AND TOOLS

2.1. Theory: Statistical mechanics and thermodynamics

At and close to equilibrium self- and directed assembly can be described by the second law of thermodynamics, whereby the system free energy is minimized. For instance, in the canonical ensemble, i.e. constant number of particles, constant volume and constant temperature, the Helmholtz free energy $F = U - TS$ is minimized, where U is potential energy, T is temperature and S is entropy [14, 15]. Starting from any initial configuration, the system will evolve so that U is decreased and S is increased simultaneously. In principle, the building blocks will eventually form a thermodynamically stable structure, the morphology of which is determined by the competition between the energetic term, U, and entropic term, $-TS$. The entropic term dominates at high temperature. As temperature is lowered, the energetic term becomes influential and the system exhibits certain structural ordering at the expense of the entropy. The transition from disorder to order is usually a first order phase transition. For self-assembly applications in soft matter systems, the disorder-order transition point is of particular interest.

Statistical mechanics is the most widely used tool for studying the phase transition occurred in self-assembly processes. In the statistical mechanics framework, macroscopic properties are computed based on the collection of microscopic configurations of assembling building blocks, which are sampled with relevant probability distributions [14, 15]. Specifically, the expected value of a macroscopic quantity A is computed from the weighted average: $\langle A \rangle = \Sigma A P(A)$, where $P(A)$ is the probability of observing the configurations with A and the sum is performed over all the sampled configurations. The key assumption here is that the building block system of interest is at equilibrium with the surrounding environment under certain thermodynamic constraints, e.g., constant temperature, or constant temperature-constant pressure or constant chemical potential. The fundamental challenge to statistical mechanics-based methods is to yield statistically accurate results, particularly when the free energy landscape is generally unknown *a priori*. For directed assembly processes that are away of equilibrium, such as those induced by evaporation, shear flows and electrical field, non-equilibrium statistical thermodynamics techniques will be required [15].

2.2. Design approaches

Numerous approaches to designing nanostructures from bottom up have been proposed and employed in the past decade. In the inverse statistical mechanics approach, the goal is to find the optimal parameter set for the interaction between the building blocks, which presumably has a known analytical form, that leads to a given target structure [16-18]. The optimized interaction is tested by molecular simulation to check if the target structure results. The challenge with this approach is to realize the obtained interaction in experiment. Another route is to propose the candidate phases (often crystalline phases) and then perform free energy calculations to find the thermodynamically most stable structure [19-21]. Alternatively, molecular simulation is employed with the physical models of the building blocks interacting based on van der Waals and Coulombic interactions. The relevant control parameters such as concentration, temperature, pressure, building block geometry and interaction strength are varied. This approach has become routine in practice for several reasons. First, the physical models can be justified by experiment. Second, the design space can be explored efficiently by varying the control parameters systematically. Finally, simulation is useful to explore regions of the parameter space that are inaccessible by experiment at the time.

2.3. Methods: Molecular Dynamics and Monte Carlo simulations

Particle-based simulation methods can be roughly classified into two families: Molecular Dynamics (MD)-based and Monte Carlo (MC)-based methods. MD and MD-based methods such as Brownian Dynamics (BD) and dissipative particle dynamics (DPD) sample microstates by integrating the Newtonian equation of motion of all the particles under thermodynamic constraints. For mesoscopic simulation methods such as BD and DPD, the equations of motion of individual particles are stochastic as they include additional terms representing the collective effects of implicit solvent molecules and counterions on the particles. Meanwhile, MC-based methods sample the system configurations using *a priori* probability distributions. For instance, most conventional MC methods employ the Metropolis acceptance criteria, which are based on the Boltzmann distribution. Hybrid MD/MC methods have also been developed to maximize their advantages [22]. We should note that simulation methods that couple MD with quantum mechanical calculations such as *ab initio* MD simulations and quantum mechanics/molecular mechanics (QM/MM) are also widely used in computational materials design but are beyond the scope of this report.

Molecular simulation methods are developed based on statistical mechanics [23-25], which connects macroscopic observables such as temperature, density and free energies to statistics of microscopic configurations. Particularly, in conventional MD and MC methods, when the number of sampled configurations is sufficiently large, the probability of observing microstates with energy E at temperature T is proportional to $P(E, T) \sim \Omega(E) \exp(-E/k_BT)$, where is $\Omega(E)$ the density of states, k_B is the Boltzmann constant and T is temperature. The sampling process is governed by the Boltzmann factor, $\exp(-E/k_BT)$. For studies on non-equilibrium processes and rare-event kinetics [26, 27] and those involving free energy calculations [28], state-of-the-art methods are often needed, as will be described below. The optimal simulation method for a specific problem is of course strongly dependent upon the length and time scales of the phenomena of interest as well as the questions to be addressed. Interested readers are referred to classical textbooks such as Refs. [23-25] for thorough discussion.

While molecular simulation is clearly a powerful tool, care should be taken by its practitioners [29]. It is evident that the physical model determines if the extent to which simulation results are relevant to the actual system. Meanwhile, the chosen simulation method often influences the statistical accuracy of the simulation results and computational efficiency. For example, if the objective is to predict the ordered structures assembled at low temperatures and/or with strong attractive forces between the building blocks, using conventional brute-force MD (or MC) simulations would not help because the system will be kinetically arrested in disordered metastable states. To mitigate the negative effects due to kinetic effects, most studies resort to either (1) running multiple simulations from different initial configurations and/or (2) cooling the system slowly step by step in temperature and combining annealing with cooling. The first approach helps ascertain that the results are not biased by initial conditions, and the second helps the system relax at each intermediate temperature and hence more likely escape from kinetic traps. In many cases, advanced sampling techniques such as umbrella sampling, replica exchange and non-Boltzmann sampling should be employed to improve the statistical accuracy of the sampling process [24, 25, 28]. Techniques that generate overlapping distributions and flat-histograms of the order parameters (or reaction coordinates) typically invoke conventional MD or MC simulations as their sampling engines, adding biasing forces/potentials to the particles so that the system can overcome high energy barriers that are unknown *a priori*.

2.4. Simulation software and data analysis tools

In 1957 Alder and Wainwright [30] conducted the first Molecular Dynamics simulation study with 32 hard spheres in a cubic box. Since then, molecular simulation has benefitted from the enormous progress made in algorithms, software engineering and computer hardware. MD simulations of hundreds of nanometers and nanoseconds have become routine on medium-sized clusters and supercomputers. For materials design studies, advances in multiscale modeling, sampling techniques and scientific computing have accelerated the investigation of assembled structures, characterization of their properties and analysis of their responses to external fields.

The primary interactions between the assembling building blocks at nano- and mesoscales, such as van der Waals forces, Coulombic interactions and hydrophobic/hydrophilic interactions, are non-covalent in nature. Van der Waals interactions decay with $1/r^6$, where r is the distance between particles. Coulombic interactions between charged particles, if screened by medium polarizability and ionic strength, decay exponentially with r or substantially faster than $1/r^3$. These interactions are short-ranged, meaning that a particle only interacts with neighboring particles within a certain distance, usually in the same order of magnitude as its size. In low dielectric constant media, however, electrostatic interactions are weakly screened and special techniques are required to evaluate the long-range contributions to the particle forces and Coulombic potential energy. Widely used techniques such as particle-mesh Ewald (PME) and particle-particle particle-mesh (PPPM) compute the long-range contributions in the reciprocal space using Fourier transformations, the computational complexity of which are $O(N\log(N))$, where N is the number of charged particles. Alternatively, one can use multipole expansion methods, which yield better scaling, i.e. $O(N)$, for large scale systems [23, 24]. It is the non-covalent nature of these interactions that enables the development of coarse-grained models to improve the computational efficiency while preserving the key physics of the phenomena of interest.

Because of the short-ranged nature of the interactions in coarse-grained models, force and energy computation can be performed concurrently by a large number of processing units. Efforts for parallelizing MD simulations have been developed since the 1980s and greatly improved along with the advances in computer engineering. Parallel algorithms for MC simulations have been rather limited mostly due to the sequential nature of the statistical sampling methods. Nonetheless, recent efforts have shown promising approaches for speeding up large-scale off-lattice simulations using fine-grained parallelism [31]. Popular open-source molecular simulation codes in the field such as GROMACS [32], AMBER [33], DLPOLY [34], MCCCS Towhee [35], LAMMPS [36], NAMD [37], Desmond [38], and recently, HOOMD-Blue [39, 40] and OpenMM [41] all support multiple parallelization options. The advantages of using these software package include verified accuracy and reliability, high computational efficiency, regularly maintained and upgraded functionalities. More importantly, the use of the same simulation code and workflow allows for data reproducibility, which is crucial for data-driven materials design approaches.

Over the last two decades, the rapid development in computer engineering and parallel computing techniques has boosted the performance of molecular simulation codes substantially. With the performance of traditional multi-core central processing units (CPUs) being capped by the transistor density and cooling issues, the use of accelerators such as general-purpose graphics processing units (GPGPUs) and many-core coprocessors has been growing steadily. GPGPUs, in fact, are now having a considerable share in scientific computing because of the availability of free-of-charge software libraries such as NVIDIA's CUDA and the OpenCL framework. When the most time-consuming tasks in molecular simulation, i.e. force and energy computation, are implemented to exploit the fine-grained parallelism provided by these coprocessors, it is evident

that simulations become substantially faster than earlier. For instance, using HOOMD-Blue v2.2 a simulation of a block copolymer melt consisting of 64000 particles (a typical size nowadays) run on an Intel Xeon E5-2680 v4 CPU coupled with an NVIDIA Tesla P100 GPU is an order of magnitude faster than the CPU-only runs [40]. Newer generations of NVIDIA GPUs generally offer better speedup as the number of streaming processors, core clock rate and memory bandwidth are all increased.

The greatly improved performance of the simulation enables investigation of much larger system sizes and much longer simulations and allows for launching more simulations given a certain time frame. By doing so, we can exclude finite size effects as well as enhance statistical accuracy of the simulation results. As the amount of data produced is proportionally increased, it is important to realize the roles of data storage facilities and data analysis software. In offline analysis, i.e. simulation output data is written to, and read from, hard drives and analyzed independent of the simulation runs. For large data sets (up to several terabytes), state-of-the-art visualization and analysis software packages, such as VMD [42] and VisIt [43], are usually needed because they support parallel data input/output (I/O) across multiple compute nodes and with GPU acceleration. VMD also supports scripting through the Tcl/Tk interface, allowing for batch processing in text mode, which proves useful for handling a large number of frames on data storage compute nodes. For online analysis, i.e., analyzing data during the course of simulation runs, there is no need to produce a large amount data on the hard drives but it is up to the capacity of the simulation packages. Open-source codes like LAMMPS and HOOMD-Blue provide a programming interface for users to implement their customized online analysis tools as extensions to the main codes.

For self-assembly studies it is often necessary to characterize the structural properties of the system during the course of the assembly process. The local ordering of the building blocks within the structures can be characterized by certain metrics. A natural metrics is the system potential energy, which decreases upon the aggregation of the building blocks. However, potential energy may be rather insensitive with regards to how the building blocks orient with each other. For instance, to monitor the alignment of liquid crystal molecules in nematic or smectic phases, the nematic order parameter, P_2, is often used. P_2 is defined as the largest eigenvalue of the 3 by 3 matrix, $p_{\alpha\beta} = \langle 3u_\alpha^{(i)} u_\beta^{(i)} - \delta_{\alpha\beta} \rangle/2$, $\mathbf{u}^{(i)} = [u_x^{(i)}, u_y^{(i)}, u_z^{(i)}]$ where is the unit length director of the rod-like particle i; α, $\beta = x$, y, z; $\delta_{\alpha\beta}$ is the Kronecker delta, and $\langle \cdot \rangle$ represents the time averaging over all the particles in the system. P_2 varies from zero to unity, corresponding to an isotropic phase and a nematic phase with a preferential aligned direction of the directors, respectively. It is possible to combine multiple relevant metrics into a shape descriptor, or more generally, a morphology feature, for more sophisticated structures [44, 45]. If two shape descriptor instances can be quantified to distinguish two phases, one can identify the obtained structure from simulation with those in a reference library. Shape descriptors can also be used for monitoring the self-assembly process toward a target structure can be monitored, and mapping phase diagrams automatically [44-46]. Specifically, state points with similar shape descriptors are grouped into the same phase, reminiscent of the k-nearest neighbor (KNN) algorithm used in statistical modeling and pattern recognition [47]. Note that this is where data science concepts and techniques (e.g., shape descriptors, data mining and machine learning) prove helpful for materials science problems.

Given the well-established foundation of simulation methodology and the dramatically increased capacity of simulation software and data analysis tools, it is interesting to see how computer simulation has benefited the design of nanomaterials using bottom up approaches such as self-assembly over the past decades. In the following sections, we will show that computer

simulation can provide not only novel insights into intriguing experimental results, but also reliable predictions to motivate ongoing experiments.

3. MODELING EXPERIMENTAL SYSTEMS

Advances in synthetic techniques maturing over the past decades have led to nano building blocks of a wide variety of materials including metallic nanoparticles, semiconductors, polymers and biomolecules and their composites [9, 11]. Also reported are assembled nanostructures in a broad range of morphologies and complexity, ranging from cubic-centered phases, hexagonally packed cylinders, double gyroids and lamellae as regularly seen with block copolymers (see Ref. [48] and the references therein) to crystalline structures [49, 50] to superlattices by mixtures of colloids [51, 52] and superstructures [53-58]. The assembly processes span multiple length and time scales from atomic to molecular to mesoscopic scales, i.e., from tens of Angstroms to hundreds of nanometers in length and from nanoseconds to microseconds in time. It is the diversity in assembling systems and the broad spectrum of spatial and temporal scales that pose fundamental challenges to experiment as to understand the assembly mechanisms and to predict the resulting structures. Moreover, impurities, polydispersity and non-equilibrium effects are in many cases avoidable factors that make the realization of the key physics of the systems of interest much difficult in experiment.
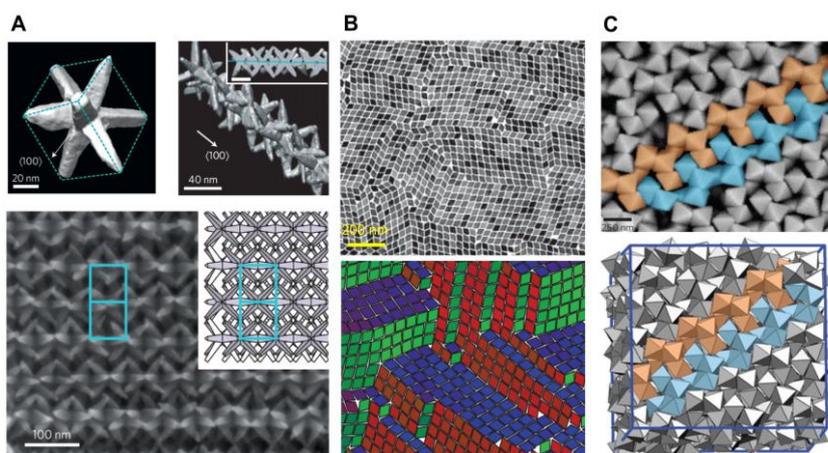

Figure 1. Simulation corroborating experimental results: (A) Superstructures formed by octopod-shaped nanoparticles: an isolated particle (top left); a linear chain from interlocking particles (top right). Bottom: linear chains packing side by side to form the superstructure. The structure predicted by simulation is shown in the inset. Reprinted from Ref. [59] with permission. Copyright 2011 Springer Nature. (B) Assembled structure by rhombic nanoplates from experiment (top) and from MC simulation (bottom). Reprinted from Ref. [60] with permission. Copyright 2013 Springer Nature. (C) Superlattice assembled by octahedral-shaped silver nanoparticles in experiment (top) and MC simulation (bottom). The highlighted particles reveal their local packing in the superlattice. Reprinted from Ref. [61] with permission. Copyright 2012 Springer Nature.

To address such fundamental challenges, coarse-grained (CG) models are often developed so to capture the essential physics relevant to the relevant length and time scales of the self-assembly process. CG models are essentially a more compact representation of the actual systems, where high frequency degrees of freedom are averaged out so that molecular simulation, energy minimization and stability analysis can be performed more efficiently. In

many cases, advanced techniques are needed for developing CG models from higher-resolution models, i.e. at quantum mechanical and all-atom levels [62]. Given a suitable model molecular simulation and numerical analysis can help elucidate the mechanism of intriguing processes, which appear nontrivial with experimental approaches alone. As an instance, Miszta *et al.* used simulation to explain how octopod-shaped nanoparticles into complex superstructures as shown in Figure 1A [59]. They showed that the particles assemble into dimers, which are more kinetically accessible than other competing configurations, to minimize their van der Waals attraction. The dimers subsequently grow at two ends where additional particles are entropically favored to attach to form chains. The linear chains then align and pack into the final structure to maximize translational entropy. Here nanoscale modeling and simulation provide insights into the influences of the irregular building block geometry on the local packing and assembly pathway toward the assembled structure.

Another type of hierarchical assembly of nano building blocks that has also been of great interest is the formation of terminal supraparticles, i.e. self-limited clusters with a uniform size. The formation of these terminal assemblies has been experimentally shown to be consistent for various systems including semiconductors [58] and mixtures of semiconductors and proteins [63]. Understanding the mechanism of this type of hierarchical assembly is therefore vital as we want to precisely control the dimension of the assembled clusters. By developing generic phenomenological models that captures the renormalized repulsion between the building blocks when they aggregate, we have shown that the self-limited organization of such supraparticles results from the balance between the on-the-fly renormalized repulsion and the short-ranged attraction between the building blocks [64]. The model also explains why the reduced size polydispersity of the assemblies even when the assembling building blocks are considerably polydisperse in size, as observed in experiment.

Multiscale modeling is often required when chemical specificity plays important roles. In the experiment by Murray group [60], it was found that highly faceted planar lanthanide fluoride nanocrystals assemble into regularly ordered structures at the liquid-air interface (Figure 1B). Note that the nanocrystals have a highly faceted shape. The authors first performed first-principle calculations with atomic-level details to find that the nanocrystals are more attractive to each other at the edges. They then conducted MC simulations on a coarse-grained model of the nanocrystals, showing that the edge-edge attraction and shape anisotropy are key factors that lead to the ordered structure observed in experiment. As another example, experimental studies showed that silver nanocrystals in various polyhedral shapes assemble into their theoretically predicted densest packings, except those with an octahedral shape (Figure 1C) [61]. The octahedral-shaped nanocrystals form a superlattice with a previously unknown packing pattern composed of two distinct motifs: lines and counter-rotating helices. Using a CG model and Monte Carlo simulations, Henzie *et al.* demonstrated that it is the depletion attractions between the octahedra that are responsible for the formation of such motifs. Further examples of self-assembly studies that involve both experimental and computational efforts can be found in Refs. [54, 58, 65-67].

4. COMPUTATIONAL DESIGN OF NEW MATERIALS

Compared to experimental studies, which are limited by accessible synthetic techniques at the time, computational studies allow for much flexibility because in principle there are no constraints in "computer experiments". Predictions from simulation can at the very lease be useful for experimental studies as to provide qualitative behaviors of the systems under investigation. In simulation studies, systematic investigation of control parameters such as

temperature, concentration and building block geometry can be done straightforwardly. Typically, the predictions from simulation are summarized in the form of "phase diagrams", which show the relationship between the control parameters and the resulting morphologies. Phase diagrams of metallic alloys, block copolymers [68] and liquid crystals [69] are among the most popular examples, where the phases are reported with respect to thermodynamic parameters such as pressure versus density or temperature versus volume fraction.
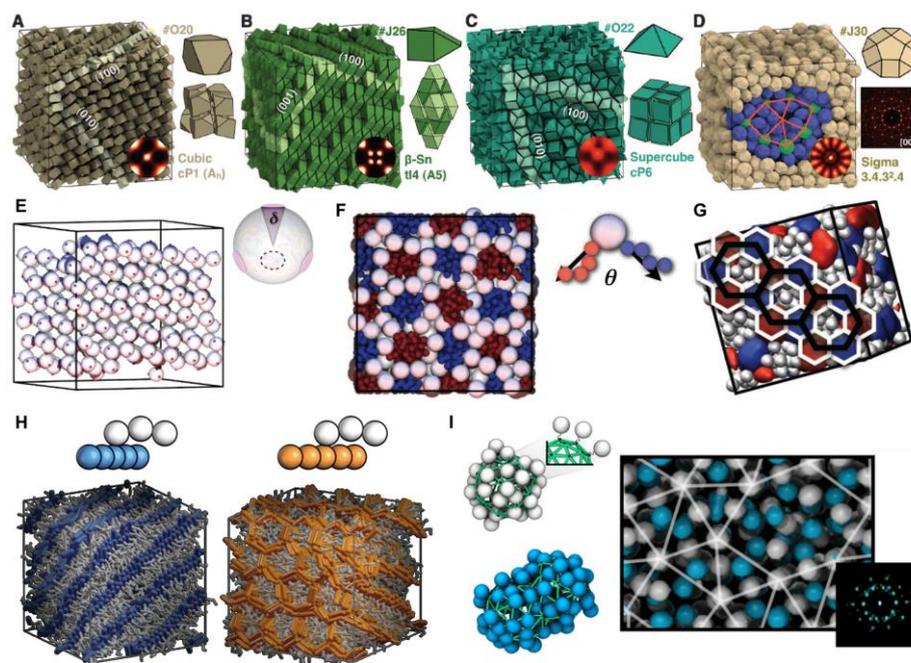

Figure 2. Assembled morphologies predicted by computer simulation: (A-D) Polyhedra forming various complex crystal and quasicrystal phases. The phases are entropically stabilized by the particle shape anisotropy. Reprinted from Ref. [70] with permission. Copyright 2012 Science. (E) Patchy particles assembling into a diamond crystalline structure. Reprinted from Ref. [71] with permission. Copyright 2005 American Chemical Society. (F-G) Polymer-tethered nanospheres with different angles, θ, between the tethers forming tetragonally and [6;6;6] columnar structures. Reprinted from Ref. [72] with permission. Copyright 2009 American Chemical Society. (H) Polymer tethered nanorods forming bilayer sheets and honeycomb grid assemblies. Reprinted from Ref. [73] with permission. Copyright 2010 American Chemical Society. (I) Spherical and elongated micelles self-assembling into a dodecagonal quasicrystal approximant. Reprinted from Ref. [74] with permission. Copyright 2011 National Academy of Sciences.

In addition to thermodynamic parameters, the building block anisotropy opens new horizons to designing materials from bottom up. Glotzer and Solomon [75] in 2007 proposed a generic framework in which building block anisotropy in terms of shape, aspect ratio, patchiness and faceting are the new "knobs", with which nanostructures with arbitrary complexity can be achieved. Figures 2A-E show several examples of the assembled structures predicted by simulation. An interesting approach to tuning anisotropy is to functionalize nanoparticles and colloids with immiscible polymers or DNAs [72, 76-80] (Figures 2F-I). Note that the resulting morphologies, e.g., micelles, hexagonally packed cylinders, perforated lamellae and lamellar phases, resemble those observed with block copolymers and liquid crystal molecules. The rich phase behavior is attributed to the immiscibility between the nanoparticles and the tethers and

the local packing governed by the shape of the nanoparticles. Remarkably, certain assembled structures were shown to reconfigure from one to another in response to minor changes in the particle geometry. For instance, the bilayer sheets assembled by polymer-tethered nanorods transition into the honeycomb grid upon lengthening the rod segments, and vice versa (Figure 2H) [73]. Higher-order assemblies, such as terminal clusters [81] and unusual complex crystals and quasicrystals [20, 70, 82, 83], are predicted to form by patchy particles, Janus particles and faceted polyhedra. MD simulation also predicted that a dodecagonal quasicrystal approximant could form in a mixture of spherical and elongated micelles (Figure 2I) [74], which is to be realized in experiment.
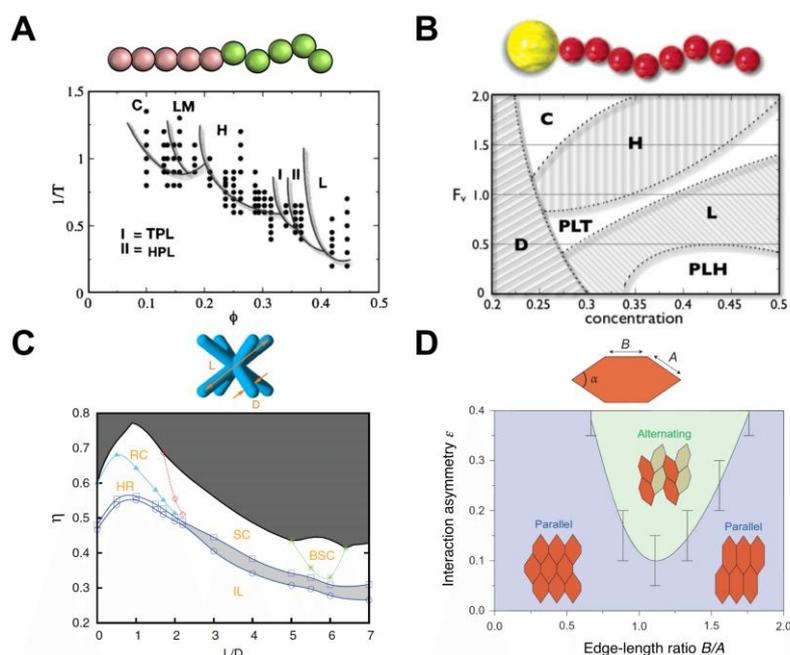

Figure 3. Examples of the phase diagrams predicted by MD and MC simulations: (A) End-tethered nanorods in solution forming body-centered cubic micelles (BCC), long micelles (LM), hexagonally ordered chiral cylinders (H), tetragonally and hexagonally perforated lamellae (TPL, HPL), and smectic C lamellae (L). Reprinted from Ref. [84], with the permission of AIP Publishing. (B) Polymer-tethered nanospheres forming lamellae (L), perforated lamellae through the headgroup (PLH), hexagonally packed cylinders (H), perforated lamellae through tethers (PLT), cubic ordered spherical micelles (C) and disordered phases (D). F_v is the excluded volume ratio of the nanosphere (yellow) versus the tail (red spheres). Reprinted from Ref. [85] with permission. Copyright 2005 American Chemical Society. (C) Octapod-shape colloidal particles in slab confinement forming stable square-lattice crystal (SC), binary-lattice square crystal (BSC), rhombic crystal (RC), and hexagonal plastic crystal (HR) phases. *L/D* is the length-to-diameter ratio and ϕ is the volume fraction of the colloidal particles. Reprinted from Ref. [20] with the permission of AIP Publishing. (D) Phase diagram of the nanoplates in 2D as a function of edge-length ratio *B/A* and interaction asymmetry ε from MC simulation. Reprinted from Ref. [60] with permission. Copyright 2012 Springer Nature.

Typical phase diagrams obtained by molecular simulation are shown in Figure 3. Horsch and coworkers using Brownian Dynamics simulation found that polymer-tethered nanorods in a solvent poor to the rods while good for the polymeric tethers, exhibit an interesting phase behavior [84]. The phase diagram in Figure 3A summarized their findings, showing the dependence of the assembled nanostructures upon inverse temperature and concentration. Shown

in Figure 3B is the phase diagram obtained by Iacovella *et al.* for the assembly of nanospheres functionalized with one polymeric tether in a selective solvent. They predicted that the polymer-tethered nanospheres would assemble into lamellae, perforated lamellae and BCC spherical micelles when the spheres are solvophobic and the tethers are solvophilic [85]. In the third example (Figure 3C), using Monte Carlo simulation Qi *et al.* [20] predicted that colloidal particles with an octopod shape form numerous crystalline structures on a flat substrate. Indeed, all the rhombic crystal, square-lattice crystal and binary lattice square crystal were observed in experiment [65]. In the last example, the phase diagram in Figure 3D showed that the arrangement of the nanoplates are dependent upon the edge length ratio and interaction asymmetry, which correlates well with experimental results [60]. The interaction asymmetry is defined as $\varepsilon = (2\xi_{A\text{-}B}/(\xi_{A\text{-}A}+\xi_{B\text{-}B})-1)$, where $\xi_{A\text{-}A}$ and $\xi_{B\text{-}B}$ are the attraction strength between like edges and $\xi_{A\text{-}B}$ is the attraction strength between unlike edges. The formation of the alternating arrangement of the nanoplates at the certain range of the edge-length ratio and with sufficient interaction asymmetry is attributed to the fact that this is the energetically favorable configuration that maximizes the contacts between unlike edges. The above discussed studies confirm that the building block geometry, the sticky patches and the density of the grafted tethers all play important roles in dictating the assembled morphologies. Importantly, computer simulation can offer predictions to the design of a wide range of nanostructures, which can be tested by experiment.

We conclude our discussion with recent studies on shape-programmable particles and active matter. Inspired by biological macromolecules, which are able to adopt various conformations in response to their environment, efforts are devoted to fabricating building blocks that can transition between different shapes in a controllable manner [86-88]. Janus micro-cylinders made from poly-(lactic-co-glycolic acid) (PLGA) take on various anisotropic geometries upon heating or cooling [86]. This family of shape-shifting building blocks offers interesting options for bottom up design such as faster assembly processes with fewer defects and unconventional pathways, which are inaccessible from static building blocks [73, 89]. In this perspective, both thermodynamics and kinetics are key to the robust formation of the target structures [90]. Meanwhile, active matter such as self-propelled building blocks, which continuously convert input energy, e.g., via internal chemical reactions, into their motion [91]. With these autonomous building blocks come the possibilities of dynamic assembly where assembled structures are able to reconfigure to optimize their functions. Certainly, novel theoretical and computational techniques are required for such out-of- and or far-from-equilibrium processes [92, 93].

5. CONCLUSIONS

Molecular simulation has been playing an increasingly important role in nanoscience, and it is now common for high-impact, groundbreaking studies to embrace simulation to elucidate experimental findings. For self-assembly studies in particular, computer simulation corroborates experimental observations by providing insights into the assembly process at microscopic levels, as well as the thermodynamic stability of assembled structures. With regards to materials design, computer simulation serves to accelerate the exploration of the vast landscape of the design parameters, which may be beyond theoretical and experimental capacities currently accessible. We envision that the computational results and predictions will certainly benefit future endeavors with useful databases for data mining techniques to further accelerate the discovery of new materials [47, 94, 95].

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