Assembly engineering: Materials design for the 21st century (2013 P.V. Danckwerts lecture)

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HIGHLIGHTS

- Self assembly remains an important and growing paradigm for creating materials.
- Theoretical and experimental advances are enabling structure prediction.
- The field of self-assembly has matured greatly in recent years.
- We can now move beyond the science of assembly to the engineering of assembly.
- "Assembly Engineering" will enable materials design for the 21st century.

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1. Introduction

We are in the midst of a materials revolution—a revolution in which materials will be designed, optimized, and engineered, rather than merely selected, for targeted properties, behavior, and function. Twenty-first century materials and devices will be made and tailored to target specifications, combining disparate and even competing attributes of multiple materials classes to achieve new functionality. They will be dynamic and responsive, able to reconfigure autonomously or on command, changing their appearance, strength, electronic, and other properties. Examples include reconfigurable automotive “skins” to optimize aerodynamics, smart prosthetics and bionics, shape-shifting robots, and camouflage coatings with adaptive optical properties that, through biomimicry, match surroundings to avoid detection. This intrinsic tailorable and dynamism will contrast starkly with today’s relatively static matter that is largely chosen, rather than designed, for the task at hand. Enabling this new materials paradigm is a new field we dub Assembly Engineering.\(^1\)

2. Assembly science and engineering

Assembly Science is the science of how things put themselves together (“self assemble”) into ordered arrangements (Fig. 1). Self assembly is a ubiquitous process in nature, underlying such seemingly disparate processes as protein folding, lipid membrane and virus capsid formation, freezing of water to ice, liquid crystalline behavior and the formation of complex crystals from atomic, molecular, nanoparticle and colloidal building blocks. Thermodynamics and kinetics underlie self-assembly processes: ordered

\(^1\) This same term is also used in a different context in the automotive industry.
Molecular simulation has been highly successful in discovering new types of building blocks, made in large quantities (“by the bucket”), that can self-assemble into complex, functional, morphable structures. Assembly Engineering builds upon the thermodynamic foundations of assembly science to engineer these building blocks in order to optimize the yield (quantity as well as quality) of a desired assembly. This paradigm shift is possible today due to the great strides in synthesis, characterization and computing over the past decade. New nanoparticle and colloidal building blocks, comprising organic, inorganic, and/or biological constituents, and with arbitrary shape and interaction patchiness, can now be made nearly to specification (Fig. 2) (Glotzer and Solomon, 2007; Lee et al., 2011; Sacanna and Pine, 2011; Pawar and Kretzschmar, 2010). These particles form a new class of building blocks now commonly referred to as “patchy particles” (Zhang and Glotzer, 2004), reflecting a degree of similarity and even universality among seemingly disparate systems (Glotzer and Solomon, 2007). Given this newfound ability, how can we use these novel building blocks as the “atoms” and “molecules” of tomorrow’s materials? How do we organize them into useful stuff?

To put this challenge in perspective, consider assembling a cube 2 cm on an edge from silver nanoparticles roughly 10 nm in diameter. Such a cube contains of the order of $10^{18}$ nanoparticles. Placing the nanoparticles sequentially into a lattice even at the rate of ten million per second would take more than 10,000 years. It is easy to see why self-assembly is a more attractive route.

Great strides in computing capabilities in recent years make possible the rapid exploration of vast chunks of design space required for assembly engineering. Today, graphics processors (GPUs) capable of up to four trillion floating-point operations per second on a single chip are readily available. In comparison with traditional CPUs, GPUs are significantly faster and their speed increases every year through the use of massive on-chip parallelization. Such speeds allow the rapid calculation of interparticle forces needed to simulate assembly processes of real materials. As one example, molecular dynamics simulations of the assembly of colloidal particles into crystals on a single GPU run as fast as the same simulation running on more than 100 CPUs working simultaneously via fast interconnects (codeblue.umich.edu/hoomd-blue; Anderson and Glotzer). Even inherently serial Monte Carlo simulations, appropriately parallelized, show enormous speed benefits from GPUs (Anderson et al., 2013). Beyond hardware, newly developed algorithms allow rapid, on-the-fly screening of assemblies to identify structures (Keys et al., 2011b, 2011a; Phillips and Voth, 2013) are driving advances in assembly simulations by greatly facilitating the analysis associated with the much larger data sets generated by using faster architectures.

This level of computer and algorithmic power is needed to explore efficiently the nearly infinite set of design parameters possible (Glotzer and Solomon, 2007), and to rapidly screen potential building blocks for their assembly propensity (Jankowski and Glotzer, 2012); that is, the thermodynamic and kinetic propensity to self assemble the target structure reliably and reproducibly, with high quality and high yield. Viewed as orthogonal anisotropy dimensions (Glotzer and Solomon, 2007; van Anders et al., 2014), the sets of all possible shape and interaction attributes of colloidal or nanoparticle building blocks (e.g. composition, patchiness, aspect ratio, roughness, faceting, topology, etc.) can be systematically explored using simulation in a way not possible with experimentation alone.

### 4. Design space for assembly engineering

In assembly engineering, we can group the important design parameters into four primary categories (Pelesko, 2007): building block attributes, binding forces, dynamics, and the environment (Fig. 3). As an example, consider the self-assembly of semiconducting nanoparticles into ordered structures. Experiments and simulations working together find that, under different conditions, such nanoparticles assemble into sheets (Tang et al., 2006), wires (Zhang et al., 2007), twisted ribbons (Srivastava et al., 2010), and uniform supraparticles (Xia et al., 2011) (Fig. 4). What are the four categories of design parameters in these systems?
First, the nanoparticles are made of CdTe, CdSe, or CdS. They are tetrahedrally shaped, and roughly 1.5 nm on an edge. The particles are typically coated with organic stabilizer ligands, such as DMAET or TGA. The size polydispersity of the particles varies from a few percent to 25%, depending on how they are synthesized. These are the building block attributes. Second, the interparticle forces possible in general include van der Waals forces, hydrogen bonding, electrostatic interactions due to charges on the bare particles and/or ligands, magnetic forces intrinsic to the particles, solvophobic or solvophilic forces, and entropic binding forces. Third, the particles are suspended in solution (in this case, water), and because they are small they experience Brownian forces from the solvent molecules. Brownian forces allow the particles to move around in the solvent so as to sample phase space and achieve a thermodynamic equilibrium state. Other types of dynamics are possible due to flow, sedimentation, and even self-propulsion. Finally, the particles in this case assemble in bulk solution, as opposed to on a surface. Often assembly occurs in the absence of external fields, but in the example of twisted ribbons above, light is used. These features define the environment in which the assembly takes place. By tuning various aspects of these four categories (not necessarily independently), profoundly different assemblies are possible from the same basic material system.

5. Entropy in assembly engineering

Entropy plays an important and often overlooked role in assembly science and engineering. Typically associated with disorder, instead entropy, under certain instances, can cause particles to order into complex arrangements. The thermodynamic definition of entropy arises from consideration of the number of microstates available to a system. The more microstates (think arrangements, or configurations) available to the building blocks comprising a system, the more entropy that system has. In this sense, entropy is more naturally associated with options—the more options, the more entropy (http://www.youtube.com/watch?v=chS8dpGB0E0). If a system has more microstates, then if entropy maximization is the driving thermodynamic principle, that system will order to maximize entropy. Indeed, when no other forces are involved—say, for a system of hard particles interacting solely through steric, or excluded volume, interactions—free energy minimization equates to entropy maximization in the canonical thermodynamic ensemble. Such a situation is easily achieved in colloidal suspensions when the particles are several hundred nanometers in diameter or larger, where electrostatic and van der Waals interactions are easily screened. In suspensions of smaller nanoparticles, there will typically be other forces relevant to assembly. In those cases, understanding the role of shape in the assembly process can be included by consideration of entropy as we now discuss.
The entropy-driven ordering of systems of hard rods into nematic liquid crystals (Onsager, 1949) and hard spheres into face centered cubic crystals (Alder and Wainwright, 1957; Wood and Jacobson, 1957) has been known and understood for many decades. At fixed volume fraction and temperature, hard rods sacrifice rotational degrees of freedom for translational degrees of freedom to maximize entropy of the entire system, leading to a disorder-order, nematic phase transition at a volume fraction that depends upon the particle’s aspect ratio. Under similar conditions, a random collection of hard spheres self organizes into a crystal at volume fractions above $\frac{\sqrt{2}}{3} \approx 50\%$ because there is more “wiggle” room available to the system as a whole by doing so (Fig. 5).

This counterintuitive notion of ordering to gain entropy becomes even more profound by considering shapes more complicated than spheres and rods. Hard tetrahedra spontaneously self assemble at roughly 50% volume fraction and higher into a quasicrystal with 12-fold rotational symmetry (Fig. 6) (Akbari et al., 2009). Quasicrystals – aperiodic crystals with orientational but no translational symmetry – are most often observed in metal alloys, but have been reported in a growing number of soft matter systems (Iacovella et al., 2011) including micelle, dendrimer, block copolymer, and binary nanoparticle systems. All of these are believed to result from entropy maximization considerations (Iacovella et al., 2011). The hard tetrahedron quasicrystal was the first example of a quasicrystal formed from hard particles and, perhaps more importantly, the most complex structure ever predicted for hard particles. Its discovery begs the question, “Is this finding merely an isolated example of complexity arising from entropy, or is it just the tip of the iceberg?” What other crystal structures are possible by judiciously engineering particle shape? Is it possible, through particle shape and entropy alone, to assemble colloidal crystals isostructural to every known atomic crystal, of every possible space group?

A study of 145 different polyhedrally shaped hard particles showed that the quasicrystal discovery was in fact merely the tip of the iceberg (Damasceno et al., 2012b). Monte Carlo simulations of the self-assembly of each shape predicts that 101 of the studied shapes should crystallize into crystals, rotator crystals, or liquid crystals. The rest were not observed to crystallize, possibly because no thermodynamically stable crystal exists at the volume fractions studied, or because kinetically the systems were unable to access the crystal due to jamming. Many of the crystal structures observed were complex, including crystals with up to 52 particles in the unit cell. That such complex structures are possible solely from entropy had not previously been expected.
With the abundance of data possible from such a broad study of particle shape and assembly, trends can be observed and used to engineer assemblies. For example, comparing the local particle environment via coordination number in the fluid just prior to assembly with that in the crystal, a nearly one-to-one correspondence was observed, suggesting that – though disordered on the scale of the system – the dense fluid is locally ordered in an arrangement consistent with that of the crystal (Damasceno et al., 2012b). Moreover, a comparison of particle shape via the isoperimetric quotient vs. local fluid structure revealed important trends (Damasceno et al., 2012b). Relatively non-spherical, higher aspect-ratio particles tend to form liquid crystals. Highly spherical particles form rotator crystals with large first neighbor shells where the particle centers lie on a lattice but the particles rotate about their centers. The observed rotator crystals included not only face-centered and body-centered cubic crystals but also complex Frank–Kasper structures with many-particle unit cells. Particle shapes of intermediate IQ, including tetrahedra, assemble into proper crystals with one to four particles in the unit cell.

The entropic ordering of particle shapes can be understood theoretically via a potential of mean force and torque (PMFT) (van Anders et al., in press; van Anders et al., 2014). This effective pair potential may be calculated from the logarithm of the easily obtained pair distribution function that measures the probability of finding a particle a given distance and orientation away from another particle, relative to that of an ideal gas. In systems of hard particles, an effective interaction arises from the osmotic pressure on a pair of particles by all other particles in the system. This osmotic pressure arises solely from entropic considerations, and is similar to that which drives depletion interactions. If each pair of particles arranges itself so as to take up the least amount of room, the rest of the system has more room to move around, hence more microstates. Thus the resulting state of the system arises from a competition between optimizing the number of microstates available to each pair and optimizing the number of microstates available to the rest of the system for every given possible configuration of the pair. By definition, then, the PMFT depends upon system density, and is to be thought of differently than an intrinsic pair potential between, say, atoms.

The effective entropic force exerted by one particle on its neighbor is easily extracted from the gradient of the effective potential. For non-spherical particles, the force is anisotropic and depending on shape can be highly directional (Damasceno et al., 2012a; Young et al., 2013). The entropic force field around a particle arising from the surrounding particles in the system produces an effective valence around the particle that reflects the degree of alignment of two particles due to complementary shape features. For example, tetrahedrally shaped particles at sufficiently high volume fractions tend to align their facets so as to maximize the system entropy (Damasceno et al., 2012a; van Anders et al., 2014). The entropic PMFT around any one particle is strongest at the centers of the facets, producing an effective “valence” of four due to the four facets (van Anders et al., 2014). At roughly 30% volume fraction, the entropic contribution to the free energy gained by alignment is 3 kT, and increases with increasing density (van Anders et al., in press). Depending on particle shape, entropic valence results in the hard particle equivalent of metallic bonding and covalent bonding (Damasceno et al., 2012b).

6. Shape and interaction engineering

Understanding how particle shape contributes to assembly allows us to tailor shape to achieve specific assembly engineering goals. For example, if we want a system of nearly spherical particles to assemble not into a close-packed structure typical of spheres but instead into a more open structure with fewer neighbors, we need only to purposefully slice facets into the particles at strategically chosen locations and of certain sizes.
The facets will induce local alignment of particles, creating a highly anisotropic local environment sufficient to induce long range ordering of the system into anisotropic structures. Further shape changes to faceted particles, such as corner and edge truncations, can drive the assembly of different structures within a given family of shapes (Damasceno et al., 2012a). Consideration of additional forces allows one to play off entropy and enthalpy to achieve unique structures through assembly engineering. In the example of CdTe nanoparticles, the tetrahedral shape of the particles inspires face-to-face alignment, which is further enhanced by van der Waals interactions, but inhibited by electrostatics. Moreover, competing dipole–dipole interactions flip the particle orientations. The resulting assemblies—e.g. wires (Zhang et al., 2007) and sheets (Tang et al., 2006)—are compromises that minimize the free energy. In assemblies of lanthanum fluoride nanoplates, the competition between entropy and enthalpy gives rise to competing tiling patterns (Ye et al., 2013a). In a mixture of rods and spheres (Ye et al., 2013b), entropy favors demixing of the shapes because the two shapes pack better with their own kind. However, anisotropic interactions at the rod tips favor embedding a hexagonally arranged layer of spheres between layers of aligned rods.

7. Conclusions and outlook

The nascent field of assembly engineering is growing rapidly with deepening understanding of the scientific assembly principles underlying ordering in many classes of building blocks. Assembly engineering is grounded in the elements of assembly science, providing a “reversing of the arrow”, so to speak, in designing building blocks specifically with a target structure in mind. New computer architectures and algorithms designed for these architectures make rapid screening, design and predictions possible in huge design spaces (Fig. 7). Like traditional forces, entropic forces are important in assembly engineering and provide additional degrees of freedom for the assembly engineer. Of course, many exciting challenges remain for the experimentalist and simulator alike. As in any simulation-based research, models are approximations of the real system. We strive to include any and all relevant physics, and figuring out what is and is not important for assembly is one of the great strengths of simulation, which can turn off and on forces, fields, etc. at will for a systematic study in a way that is difficult for experiment. Simulations typically address, at least at first cut, ideal systems of perfectly shaped particles of identical sizes. In reality, size and/or shape polydispersity and imperfections can hamper (Phillips and Glotzer, 2012; Phillips et al., 2010)–or help (Xia et al., 2011)–targeted assembly. For example, the dodecagonal quasicrystal self-assembled from hard tetrahedra can tolerate up to 10% polydispersity and still form the same (albeit messier) structure from the fluid phase. Such degree of polydispersity is substantially larger than the 3–5% now routinely possible in nanoparticle synthesis. We expect that the sensitivity of a particular structure to polydispersity in size or shape will undoubtedly depend on the structure, and may need to be considered on a case-by-case basis. New theoretical tools such as those in van Anders et al. (2014) will make quantification of this sensitivity possible.

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(http://www.youtube.com/watch?v=chS8dpGB0E0).


