

## Millimeter-scale self-assembly and its applications\*

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*Abstract:* Self-assembly is a concept familiar to chemists. In the molecular and nanoscale regimes, it is often used as a strategy in fabricating regular 3D structures—that is, crystals. Self-assembly of components with sizes in the  $\mu\text{m}$ -to- $\text{mm}$  range is less familiar to chemists; this type of self-assembly may, however, become technologically important in the future. In this size range, self-assembly offers methods to form regular 3D structures from components too small or too numerous to be manipulated by other means, and methods to incorporate function into these structures; it also offers simplicity and economy.

This paper focuses on the use of self-assembly to build functional systems of components with sizes in the range from microns to millimeters. It compares the principles of self-assembly at the molecular and millimeter scales, reviews the possible applications of meso-scale, self-assembled systems, and outlines some of the most important issues in the use of self-assembly to build functional systems.

### INTRODUCTION

*Molecular* self-assembly is familiar to chemists, both in molecular chemistry (e.g., the formation of hydrogen-bonded aggregates [1], molecular crystals [2], and phase-separated polymers [3]), and in molecular biology (e.g., the association of ligands and proteins [4], the formation of lipid bilayers [5], and the folding of proteins [6]). Self-assembly of *nanosized* components (e.g., nanowires and nanotubes [7], colloidal crystals [8,9]) is emerging as a subfield of materials science. Self-assembly of larger components—those with sizes in the  $\mu\text{m}$ -to- $\text{mm}$  range—is scientifically interesting, and has the potential to be technologically important. The areas of nano- and  $\text{mm}$ -scale self-assembly (mesoscale self-assembly, or MESA) are both developing rapidly, and are based, in significant part, on an understanding of *principles* derived from studies of molecular systems.

MESA has three advantages over molecular self-assembly, as an area for study and application: (i) It is often simpler to fabricate components with sizes in the range 0.1–1 mm than it is to synthesize molecules. Photo- and soft lithography, in particular, offer versatile methods for the fabrication of features with dimensions  $\geq 1 \mu\text{m}$  [10,11]. It is straightforward to observe the process of self-assembly and to characterize its products. (ii) The wide range of interactions possible between  $\text{mm}$ -sized components offers more control over the strength, range and selectivity of these interactions than do interactions important in molecular systems. (iii) In some potential types of applications,  $\mu\text{m}$ – $\text{mm}$  sizes of the components may be *required* to generate functional structures, e.g., in fabrication of electrical circuitry, electronic devices, and optical materials. Molecules do not (yet) offer the same functionality: a mole-

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cule will not be an electrical circuit in the near future. Self-assembly of  $\mu\text{m}$ -to- $\text{mm}$ -sized components fabricated using planar techniques also offers a route to 3D structures.

Our program has focused on the use of self-assembly to build functional systems of components with sizes from microns to millimeters. Here we discuss the differences and similarities between molecular and  $\text{mm}$ -scale self-assembly, and outline some of the most important unresolved issues in the use of self-assembly to build electrically and optically functional systems.

## COMPARISON OF MILLIMETER-SCALE AND MOLECULAR SELF-ASSEMBLY

Although the broad principles of self-assembly are similar for components that range in size from molecular to macroscopic, the details differ [12]:

- *Size and number of components.* Mesoscale systems contain  $10\text{--}10^4$   $\text{mm}$ -scale components, while molecular scale systems might involve  $10^{20}$  molecules.
- *Fabrication/synthesis of components.* Chemical synthesis—the method used for “fabrication” of components for molecular self-assembly—is a parallel process: many identical molecules can be synthesized simultaneously. Molecular synthesis is a highly developed art. Fabrication of  $\mu\text{m}$ -to- $\text{mm}$ -sized components can, in principle, be either a parallel or a serial process [10], but is much less efficient—and at this time, usually much more cumbersome—than simple molecular synthesis. The development of small components incorporating sophisticated function is just beginning.
- *Function.* Components with sizes in the  $\mu\text{m}$ -to- $\text{mm}$  range can be self-assembled into structures with optical or electrical functionality. Molecules cannot be positioned and connected into aggregates with such functionality.
- *Interactions.* Different types of interactions are used to cause self-assembly of molecules and  $\text{mm}$ -sized objects. The intermolecular interactions used in molecular self-assembly are much weaker and shorter range than those used in mesoscale self-assembly. More *types* of forces can be used in the self-assembly of  $\mu\text{m}$ -to- $\text{mm}$ -sized systems than in molecular systems.
- *Sensitivity to wall effects.* In both molecular and mesoscopic systems, wall effects extend over dimensions of  $10\text{--}100$  component layers from the walls. The *absolute* distance over which wall effects are important is thus enormously different (by  $10^6\text{--}10^7$ ) in molecular and mesoscopic systems, although the scaled length may be similar.
- *Temperature and agitation.* Molecular systems are agitated thermally, and the distribution of kinetic energies follows the Boltzmann equation [13]. Systems containing  $\mu\text{m}$ -to- $\text{mm}$ -sized components are sufficiently massive (relative to the molecules making up the solutions in which they are suspended) that they are unaffected by thermal motion; when suspended in an unstirred liquid,  $\text{mm}$ -scale objects are effectively at 0 K. The  $\text{mm}$ -scale systems require external agitation (e.g., by fluid shear or by mechanical agitation) to cause encounters between the components. We have not characterized the distribution of energies among the components under the conditions used in our experiments.
- *Reversibility or “adjustability”.* In both molecular and  $\text{mm}$ -scale self-assembled systems, the interactions between the components must be reversible (or the components able to adjust their relative positions within an aggregate) in order to achieve highly ordered structures. If components stick irreversibly upon encounter, the resulting aggregate is usually a glass rather than a crystal.

## APPLICATIONS OF MICRON-TO-MILLIMETER-SCALE SELF-ASSEMBLED SYSTEMS

There are several areas of practical interest for which self-assembly of  $\mu\text{m}$ -to- $\text{mm}$ -sized components might form the foundation (Table 1).

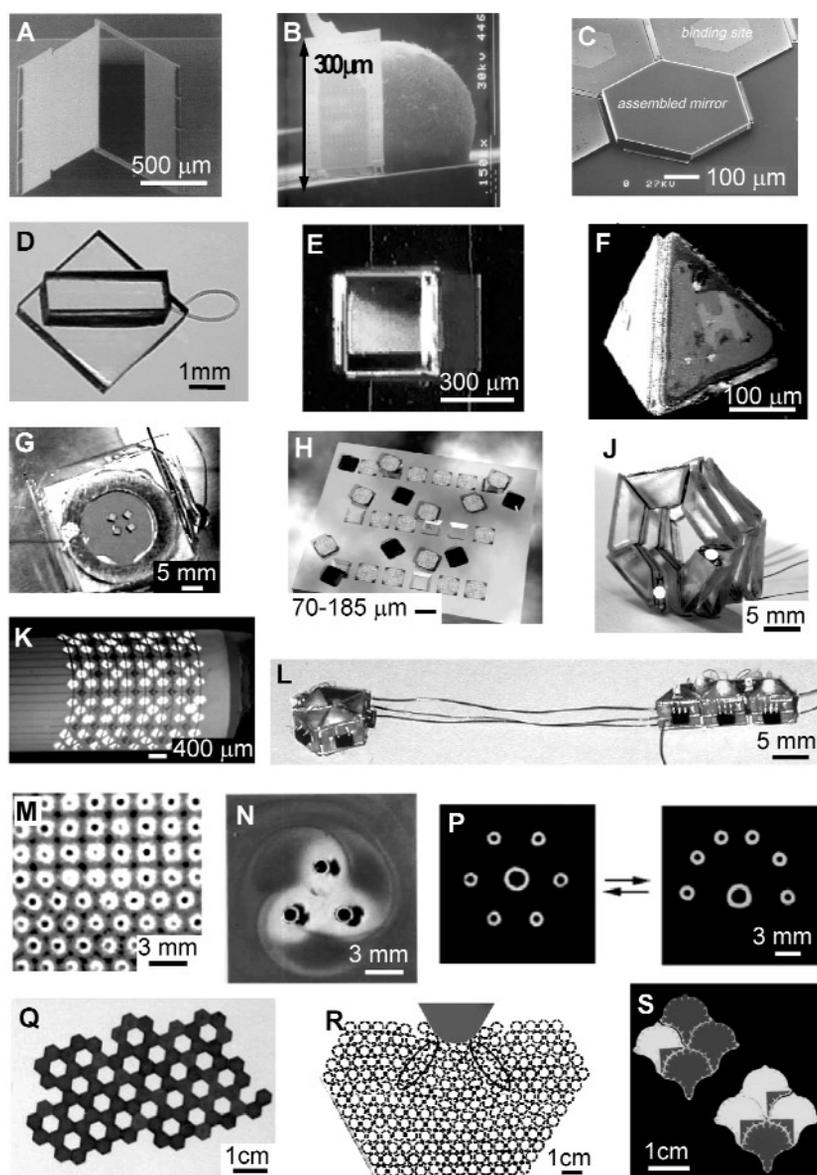
**Table 1** Examples of self-assembled functional systems.

| Demonstration   | Driving force(s)  | Reference                          |
|---|---|------------------------------------|
| <b>Fabrication of 3D structures using 2D fabrication techniques</b> |   |                                    |
| 3D structures by folding of 2D precursors                           | Capillarity<br>Electrical activation  | [17,18,20]<br>[19]                 |
| MEMS and MOEMS  | Capillarity   | [21–24,26]                         |
| <b>Demonstration of electrical and electronic function</b>          |   |                                    |
| Integrated LEDs, Si arrays  | Fluidic and gravitation<br>Vibration and gravitation<br>Magnetism<br>Electrostatic interactions | [33,37]<br>[31]<br>[34]<br>[32,35] |
| Cylindrical display   | Capillarity   | [36]                               |
| 3D electrical network   | Capillarity<br>Orthogonal capillary interactions  | [28]<br>[29]                       |
| Electronic device   | Capillarity   | [30]                               |
| Electric circuit  | Hydrophobic effect  | [27]                               |
| <b>Part orientation</b>   |   |                                    |
| Positioning of micro-mirrors  | Capillarity   | [25]                               |
| Part-to-substrate assembly  | Capillarity   | [53]                               |
| <b>Dynamic self-assembled systems</b>                               |   |                                    |
| 2D arrays   | Magnetic and hydrodynamic forces  | [39]                               |
| 2D arrays   | Magnetic and electrostatic forces   | [42]                               |
| <b>Computation</b>  |   |                                    |
| 2D arrays   | Capillarity   | [47]                               |
| <b>Models of materials</b>  |   |                                    |
| 2D arrays   | Capillarity   | [46]                               |

### Method to achieve 3D structures

The parallel fabrication of 3D structures is a major challenge for microfabrication. Microfabrication is carried out almost entirely by photolithography, and photolithography is an inherently planar technology [10].

Self-assembly is often used in the molecular and nanoscale regimes for the fabrication of 3D structures—crystals—with useful properties [14–16]. Similarly, self-assembly might provide the basis of a strategy for the fabrication of 3D structures in the micron-scale regime (Fig. 1, A–F). We and others have provided preliminary demonstrations of the fabrication of 3D structures. We fabricated planar precursors to the desired 3D shape using conventional photolithography, and patterned them with solder or polymers. Under appropriate conditions, these precursors folded spontaneously into 3D structures, with the folding driven by capillary forces between drops of liquid (polymer [17] or metal [18]), or by electrical activation of conjugated polymers [19]. This approach was loosely based on work by Syms [20] in surface tension-based assembly. This strategy is a promising, unconventional method for fabrication of microelectromechanical systems (MEMS) and microoptoelectromechanical systems (MOEMS) [21–26].



**Fig. 1** Examples of mesoscale, self-assembled structures. **A.** Asymmetric, 3D silicon micromirror formed from a planar precursor by surface tension-powered self-folding. From [49], copyright (1999) IEEE. **B.** 3D structure self-assembled from polysilicon plates using solder. Reprinted from [22], copyright (1999), with permission from Elsevier Science. **C.** Single-crystalline silicon micromirror, self-assembled onto a micromachined actuator. From [25], copyright (2001) IEEE. **D.** Polyurethane structure formed by self-assembly of a planar precursor via capillary forces. Reprinted in part with permission from [17], copyright (2002) American Chemical Society. **E.** Closed, side-mounted box self-assembled via electrically controlled folding of a planar precursor. Image courtesy of E. Smela. Reprinted with permission from [50], copyright (1995) American Association for the Advancement of Science. **F.** Patterned, metallic pyramid self-assembled from a planar substrate using solder. Reprinted with permission from [18], copyright (2002) Wiley-VCH. **G.** Surface-mount capacitors self-assembled using electrostatic force fields. From [51], copyright (1998) IEEE. **H.** Scheme illustrating the fluidic self-assembly of silicon nanoblocks into

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**Fig. 1** (*Continued*).

substrate holes of complementary shapes. Reprinted with permission from [37]. **J.** Self-assembled helical aggregate, carrying two pairs of electrically isolated wires. Reprinted with permission from [29], copyright (2002) American Institute of Physics. **K.** Cylindrical display containing 113 GaAs/GaAlAs LEDs fabricated in two self-assembly-based steps. Reprinted with permission from [36], copyright (2002) American Association for the Advancement of Science. **L.** Self-assembled electronic device, containing a ring oscillator and a shift register. From [30], copyright (2002) National Academy of Sciences, USA. **M.** Convection cells formed above a micropatterned metallic support. Reprinted with permission from [43], copyright (2001) American Institute of Physics. **N.** Aggregate of three rotating, magnetized discs interacting with one another via vortex–vortex interactions. Reprinted with permission from [38], copyright (2002) American Association for the Advancement of Science. **P.** Interconverting aggregates of magnetized discs rotating at a liquid–air interface. Reprinted by permission from Nature [39], copyright (2000) Macmillan Publishers Ltd. **Q.** Hexagons of poly(dimethylsiloxane) self-assembled into an open, hexagonal array at a liquid–liquid interface. Reprinted with permission from [52], copyright (1997) American Association for the Advancement of Science. **R.** 2D array of poly(dimethylsiloxane) objects self-assembled at a liquid–air interface, used to model indentation fracture in crystalline materials. Reprinted in part with permission from [46], copyright (2002) American Chemical Society. **S.** Acrylic tiles, self-assembled into 2D arrays at the interface of two immiscible liquids, used for computation by tiling. From [47], copyright (2000) National Academy of Sciences, USA.

**Route to 3D microelectronic systems**

Electronic devices are usually built by stacking and connecting 2D elements; their structures are thus 3D, but restricted in the types of geometries that can be generated. A true 3D microelectronic system—one with relaxed shapes and geometrical constraints—would have several characteristics that might be useful, and would certainly be worth exploring: short interconnections between the elements, high volumetric density of components, ability to fit into odd spaces, and adaptability to specific geometries (e.g., curved surfaces for displays). Since self-assembly allows manipulation and positioning of electronic components in large, ordered aggregates/arrays, it may offer a route to 3D microelectronic systems (Fig. 1, G–L).

We have demonstrated the self-assembly of a primitive electrical circuit [27], 3D electrical networks [28,29], and an asymmetrical electronic device [30]. Self-assembly has also been used to integrate electronic devices and silicon chipllets onto planar [31–35], and curved [36] substrates. The value of these systems is that they serve as demonstrations of principle and model systems, rather than as practical fabrication strategies. With the exception of the structures generated by fluidic self-assembly [37], most of the functional self-assembled microelectronic systems that have been developed to date are still too primitive to be commercialized.

**Strategy for developing simple models of energy-dissipating systems**

Dynamic self-assembled systems, i.e., systems in which the interactions between the components take place only when energy is being dissipated [38], are found at all levels of organization in living matter, and are thus of enormous interest. Simple, rationally designed macroscopic models of these complex systems would aid our understanding of the principles of dynamic self-assembly, pattern formation, complexity, and emergence. We have developed several model, dynamic, self-assembling systems based on magnetic and hydrodynamic interactions between mm-sized magnetic discs [39] (Fig. 1, N, P). These systems were also used to model chiral molecular interactions [40] and classical artificial atoms [41]. We have also explored dynamic self-assembly based on contact electrification [42] and Bénard–Marangoni convection [43] (Fig. 1, M).

## Strategy for modeling molecular systems and materials

Molecular chemistry and materials science may benefit from simple, physical models of processes taking place at the atomic or molecular levels. We have developed a self-assembling system of millimeter-sized components that organize via capillary interactions into extended, ordered, 2D arrays at a fluid–fluid or fluid–air interface [44] (Fig. 1, Q–S). This system was used to model molecular systems [45], to simulate indentation fracture in crystalline materials [46], and to compute by tiling [47]. The large size of the components, and the practicality with which their shapes and functions can be engineered, make this system a flexible alternative to previously described models, based, for example, on bubble rafts [48].

## ISSUES IN DESIGN OF FUNCTIONAL SELF-ASSEMBLING SYSTEMS

In designing functional self-assembling systems, one must consider several intertwined issues:

### Nature of the function

The first consideration when designing a functional system is the size regime that is appropriate for the desired function. Not every function is possible in every size regime; this size restriction is imposed by the physical phenomenon providing the basis for the function, or by practical limitations concerning the fabrication of functional structures. Self-assembled aggregates that function as optical elements illustrate the phenomenological restriction. The spacing in aggregates that function as optical elements must be close to the wavelength of the radiation of interest: photonic band-gap materials active in the visible region require periodicity in the range of 200–700 nm, while materials optically active in the far IR require 100 times larger periodicity [54]. Aggregates with electric connectivity or electronic function illustrate the restrictions imposed by the methods used for fabrication and connection of the components. Components with sizes between a few nanometers (e.g., organic molecules, carbon nanotubes, and semiconductor nanowires) and hundreds of microns (e.g., standard microelectronic components) can, in principle, be used to build an electronic device. While fabrication and manipulation of micron-sized components is well developed, wiring together nanoelectronic components remains a challenge [7].

### Fabrication of components

The application of self-assembly is often (in fact, usually) limited by the methods available for the fabrication of the individual components. Self-assembly seems to be a very general strategy; making components designed for optimal self-assembly may be difficult or impossible using currently available methods. There is no general pathway to fabricate small (nm– $\mu\text{m}$ ) 3D components, and the fabrication is even more complicated when the components have to carry electrical, magnetic, optical, or biological functionality. A possible strategy for fabrication of small, functional components is based on self-assembly: folding of 2D precursors into 3D shapes, or self-assembly of 2D components onto prefabricated 3D scaffolds.

Current methods of microfabrication require a compromise between the size and the complexity of the components: smaller components result in an aggregate with higher 3D density, but with lower complexity per component; larger components are easier to fabricate and can incorporate more complex function, but give a smaller volumetric density of functionality.

### Interactions between components

Self-assembly occurs when components interact with one another through a balance of attractive and repulsive interactions. In the  $\mu\text{m}$ -to-mm size range, a broader range of forces is available for use in self-

assembly than at the molecular scale (Table 2). Self-assembling systems can be designed to employ one or several types of interactions; if several, these interactions can act simultaneously or sequentially.

**Table 2** Forces of significant magnitude in the micron-to-millimeter size regime.

|                    |  |
|--------------------|--|
| Gravitational [31] | van der Waals [55]                               |
| Electrostatic [35] | Biospecific (e.g., protein:ligand, DNA:DNA) [56] |
| Magnetic [41]      | Centrifugal [57]                                 |
| Capillary [58]     | Osmotic [59]                                     |
| Fluid Shear [60]   | Entropic [61]                                    |
| Hydrodynamic [41]  | Light [62,63]                                    |
| Hydrophobic [64]   | Casimir [65]                                     |

The choice of the type of interaction(s) between components in a self-assembling functional system is based on several factors: (i) The scale and magnitude of the interactions must be appropriate for the system being considered. (ii) The interactions must be compatible with the possible/desired environment for the self-assembly: for example, magnetic forces can act in both air and in water, while hydrophobic and biospecific interactions require aqueous environments. (iii) The operation of the interactions causing self-assembly must not affect the functionality of the components: for example, magnetic fields may not be suitable for self-assembly of sensitive electronic components, and high-temperature solders can not be used with delicate biological molecules.

Most of our own work on self-assembling functional systems has used capillarity—that is, the tendency for interfaces involving fluids to minimize their areas—to cause self-assembly [44]. Capillary interactions have proved remarkably versatile: they can be tailored, they can be modeled mathematically [45,66], they are applicable to both 2D and 3D geometries, and their strength can be controlled. Molten solder is one particularly useful liquid in such systems [67]. The fact that liquid solder can be used both to cause self-assembly and to provide electrical continuity between wires on different components in a self-assembled aggregate is clearly an enormous advantage for projects dealing with self-assembling microelectronic systems.

### Connections between the components

Self-assembly can result in the formation of different types of connections between the components: functional connections (e.g., connections with electrical conductivity), structural connections (e.g., connections granting mechanical stability), or connections combining both tasks at the same time.

A key issue for the formation of functional connections is the recognition between components, governed by the design, surface chemistry, and topology of the interacting surfaces. In most man-made, self-assembling systems, the components interact via planar recognition patterns, and the assembly involves not more than two types of interactions. In contrast, the highly specific recognition and binding characteristic of biological interactions rely on interactions of multiple types, acting between complementary 3D surfaces. Future work needs to focus on developing quantitative methods for the optimized design of interacting surfaces, to ensure accuracy of binding and high yield in the process of self-assembly [25,53,68].

In addition to the design of the recognition patterns, we have identified several parameters that play a role in the formation of defects in self-assembling systems based on capillary interactions [36]. These parameters include the mode of agitation, the accuracy of fabrication of the components, the procedures for removing incorrectly assembled components, and the details of the interfacial chemistries. The level of defects intrinsic to different types of self-assembly still remains to be determined. New designs for self-assembling systems may ultimately be needed to allow self-assembly that generates complex functionality—i.e., defect-tolerant [69] or reconfigurable [70] systems.

## Biology as a source of examples, demonstrations of principle, and new concepts

Biology is the pinnacle of functional self-assembly [56]. It provides a rich set of examples of multi-functional structures with complex geometry that are formed by (bio)molecular self-assembly. Abstraction of principles of design from nature is one promising approach to the design of functional, self-assembled structures [71]. Self-assembly in biological systems produces structurally and functionally asymmetrical aggregates by using mechanisms such as hierarchical assembly, simultaneous action of multiple, different forces, folding of disordered precursors into complex 3D shapes, shape complementarity, and templating [56]. We believe that to extend the range of functions that self-assembly can achieve, all these concepts should be considered in the design of functional, self-assembled aggregates.

## CONCLUSIONS

The strength of self-assembly is its potential to generate ordered 3D aggregates of components having sizes ranging from nanometers to millimeters. As the value of this potential is increasingly recognized in micro- and nanofabrication, we have turned to millimeter-sized models to elaborate the basic principles of self-assembly. Millimeter-sized components may provide the most direct approach to a better understanding of the rules of design for self-assembling systems.

We believe that self-assembly has the potential to become one of the most useful strategies for fabrication of functional structures. The biggest obstacle to the broad use of self-assembly is not the process of assembly itself, but the fabrication of appropriately functionalized, small components. In this respect, molecular self-assembly has the advantage of being based on powerful and highly developed synthetic methods; corresponding methods still remain to be developed in the mesoscale range. Solving the problem of design and fabrication of components with sizes in the  $\mu\text{m}$ -to- $\text{mm}$  range is the key to the wider application of self-assembly in the fabrication of 3D microsystems, and in the areas of robotics, microelectronics, and netted and dynamic systems [38].

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