

Spontaneous Assembly of Magnetic LEGO Bricks

Dean J. Campbell,* Ellen R. Freidinger, Moira K. Querns

Department of Chemistry, Bradley University, Peoria, IL 61625, campbell@bradley.edu

Received July 31, 2001. Accepted August 27, 2001

Abstract: This paper describes simple methods of demonstrating macroscale spontaneous assembly. These demonstrations can illustrate topics in college or high school chemistry courses, such as the thermodynamics of crystallization and the chelate effect. The assembling units are built from a combination of magnetic and conventional LEGO building blocks. Unlike many other spontaneous-assembly experiments, these assemblies do not require surface flotation to form.

Introduction

Recent research has explored the spontaneous assembly of macroscale or visibly discernable particles. Spontaneous assembly refers to the process by which components aggregate into an organized structure without external assistance. The organizing forces are typically weak, noncovalent interactions. Self-organization or “self-assembly” of molecular species plays a role in determining the form of biochemical structures such as collagen [1], in which strands of proteins assemble into more complicated ropelike structures, and the form of two-dimensional self-assembled monolayers (SAMs) of adsorbates on solid surfaces [2].

Macroscopic or visibly distinguishable units can also spontaneously assemble. These assembly processes are being explored in the fabrication of complex physical systems and devices, especially as an alternative to conventional photolithographic techniques for building circuits [3] and to model novel computational systems [4]. In chemical education, the spontaneous assembly of bubbles [5], breakfast cereal [6], and hot dog slices [7] has been used to generate hexagonal close-packed arrays, and floating LEGO bricks have been used to generate square-type arrays [8]. Often, the visibly distinguishable units are assembled at a relatively flat liquid–liquid or air–liquid meniscus [3–13] although some assembly has been performed in three dimensions [3b, 13–15]. The attractive and repulsive driving forces behind this assembly process are based on the interactions between the units and the meniscus, also referred to as capillary interactions.

Other forces, such as magnetism, may be used to direct the assembly process [10]. Careful arrangements of magnetic poles on the units can produce either attractive or repulsive interactions between units. Units that have specific arrangements of magnetic poles can interact with each other to form specific patterns. When magnetism is used in self-assembly, liquid surfaces are unnecessary. Smooth surfaces such as glass will suffice. To overcome friction between the units or between the units and the surface, the containers holding the units are gently swirled or shaken to jostle the units past each other into truly stable patterns [9–12, 14, 15].

The thermodynamics of the spontaneous assembly process can be described by $\Delta G = \Delta H - T\Delta S$ where ΔG is the change in Gibbs energy; ΔH is the change in enthalpy; ΔS is the change in entropy; and T is not strictly the temperature (motion at the

molecular level), but rather can be a relative measure of the intensity of the shaking of the system (motion at the macroscale level). For the assembly process, ΔG and ΔS are negative. The increase in the entropy of the universe associated with all spontaneous processes is not visible within the macroscale objects themselves, but rather can be thought of as being dispersed via frictional agitation of the molecules. Because T is small (assembly only occurs when shaking is minimal), then ΔH must be negative. If T is large (intense shaking), then ΔG is positive and the reverse process (dissociation of units) is spontaneous. This same thermodynamic situation can be used to describe many crystallization and dissolution processes.

This paper describes simple methods of demonstrating macroscale spontaneous assembly. These demonstrations can illustrate topics in college and high school chemistry courses, such as the thermodynamics of crystallization and the chelate effect. The assembling units are built from magnetic and nonmagnetic LEGO bricks. The LEGO Corporation produces bricks that contain disk-shaped ceramic magnets with their poles on the flat faces of the magnets [16]. The method of magnetic assembly shown in Figure 1 uses disk magnets arranged so that their poles or (faces) are oriented up and down. With this orientation, magnets with poles pointing in the same direction will repel each other, and magnets with poles pointing in opposite directions will attract each other. One challenge in working with the LEGO magnets is that they are too strong to use by themselves. The magnets must be attached to bulkier nonmagnetic brick structures to prevent them from flipping over to attract to each other.

Figure 1a shows assemblies of units made from four 1-by-2 pegbricks arranged in a pinwheel shape with either a north-pole-topped magnet or a south-pole-topped magnet in the middle [17]. The assemblies resemble a checkerboard pattern. Ten assembly trials were performed using ten north-pole-topped units and ten south-pole-topped units. During the trials the units were placed in a flat-bottomed glass cake pan and shaken by hand until all the units had come together to form stable structures. Three types of attractive interactions predominated, as illustrated in Figure 1a. Type 1 interactions accounted for 57% of the attractive interactions, 37.6% were type 2, and 5.4% were type 3. Figure 1b shows linear

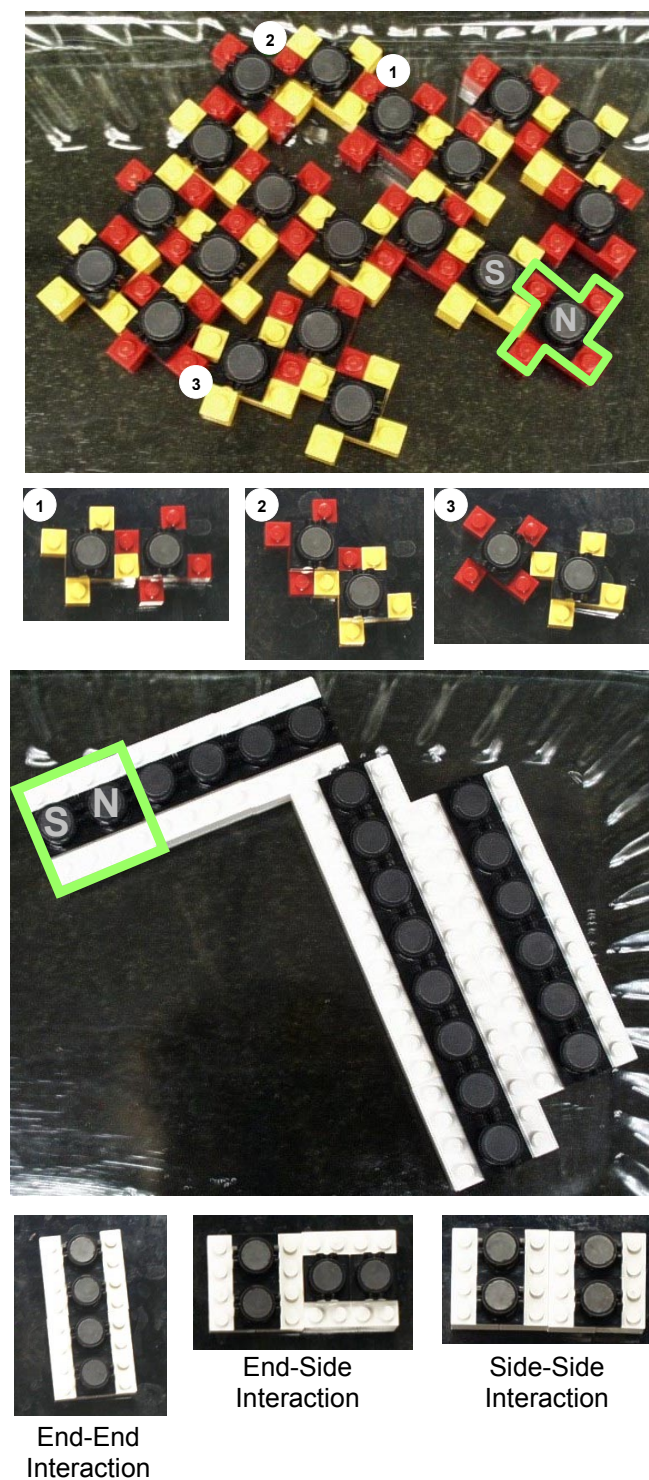


Figure 1. (a, upper) "Checkerboard" assemblies of magnetic LEGO units made from four 1-by-2 peg bricks arranged in a pinwheel shape (one is highlighted in the lower-right corner) with either a north-pole-topped magnet or a south-pole-topped magnet in the middle. (b, lower) Linear assemblies of units made from two 2-by-4 bricks with a north-pole-topped and a south-pole-topped magnet side by side in the middle of the unit (one is highlighted on the left side of the picture).

assemblies of units made from two 2-by-4 peg bricks with a north-pole-topped and a south-pole-topped magnet side by side in the middle of the unit. Out of ten trials with ten units per trial, 76.7% of the attractive interactions were end-end

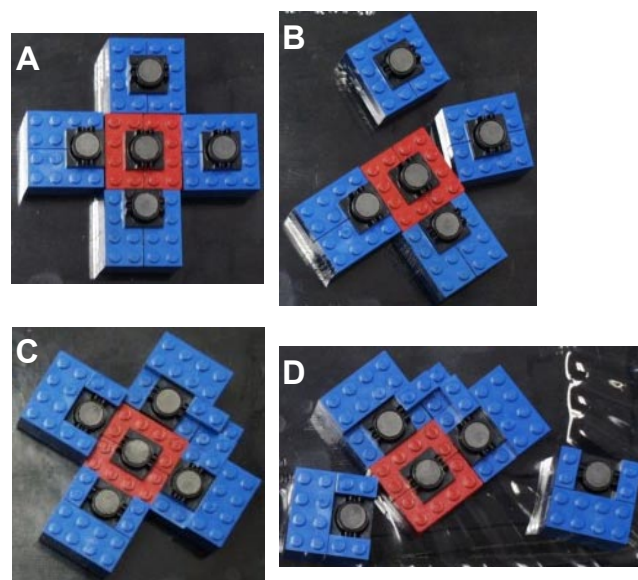


Figure 2. LEGO models of metal centers (red bricks) and ligands (blue bricks). Each metal-center magnet is pointed in the opposite direction of the ligand magnets. (A) Complex built using two strongly interacting ligands (with magnets closer to the metal center) and two weakly interacting ligands (with magnets further from the metal center). (B) Upon shaking the complex, the weakly interacting ligands tend to dissociate more readily than the strongly interacting ligands. (C) Complex built using two monodentate (one-magnet) ligands and one bidentate (two-magnet) ligand. (D) Upon shaking the complex, the monodentate ligands tend to dissociate more readily than the bidentate ligand, illustrating the chelate effect.

interactions, 17.2% were end-side interactions, and 6.0% were side-side interactions.

A variation of this assembly process can be used as an illustration of metal-ligand interactions, Figure 2. In this type of model, a magnet oriented one way can represent the positively charged metal center and other magnets oriented in the opposite direction can represent negatively charged ligands or at least the negatively charged electrons within those ligands. Figure 2a shows a metal center with two different types of ligands. One type of ligand has the magnet at the edge of the ligand; the other type has a magnet at the center of the ligand. The ligands with the magnets at their edges will be more strongly attracted to the metal center because the ligand magnets are closer to the metal-center magnet. When this assembly is placed in a 33-cm-by-23-cm glass tray and shaken at 5 Hz on an orbital shaker (Fisher Scientific, Model 361), or simply shaken by hand, the ligands with magnets in their middle tend to break away or dissociate from the metal center more readily than the more strongly binding ligands with magnets at their edges, Figure 2b. This can serve as an illustration of how different ligands can have different strengths of interaction with the same metal center. Figure 2c shows a metal center with two monodentate (one-magnet) ligands and one bidentate (two-magnet) ligand. While shaking at 5 Hz or by hand, the monodentate ligands tend to break away more readily than the bidentate ligand, Figure 2d. This can serve as an illustration of the chelate effect, in which complexes with multidentate ligands tend to be more stable than similar complexes with monodentate ligands. This effect has been explained, in part, by the increased probability of reattachment of a dissociated donor atom in a polydentate

ligand (the donor atom is still held in proximity to the metal center by the rest of the ligand). This is compared to an equivalent unattached donor atom in a monodentate ligand [18]. A similar situation appears to happen with the LEGO magnet system.

Acknowledgments. We would like to thank Bradley University and the National Science Foundation through the Materials Research Science and Engineering Center for Nanostructured Materials and Interfaces (DMR-96325227) and the LEGO Corporation for generous support.

References and Notes

- Schmitt, F. O. *Proc. Am. Philos. Soc.* **1956**, *100*, 476–486.
- For reviews on monolayer films, see (a) Bain, C. D.; Whitesides, G. M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 506. (b) Dubois, L. H.; Nuzzo, R. G. *Annu. Rev. Phys. Chem.* **1992**, *43*, 437.
- (a) Xia, Y.; Rogers, J. A.; Paul, K. E.; Whitesides, G. M. *Chem. Rev.* **1999**, *99*, 1823 provides a review of assorted methods of mesoscale and nanoscale fabrication including the use of self-assembly. b) Gracias, D. H.; Tien, J.; Breen, T. L.; Hsu, C.; Whitesides, G. M. *Science* **2000**, *289*, 1170.
- Regalado, A. *Tech. Rev.* **2000**, *103*, 80–84.
- Geselbracht, M. J.; Ellis, A. B.; Penn, R. L.; Lisensky, G. C.; Stone, D. S. *J. Chem. Educ.* **1994**, *71*, 254–261.
- Dungey, K. E. *J. Chem. Educ.* **2000**, *77*, 618.
- Campbell, D. J. Spontaneous Assembly of Hot Dogs. <http://bradley.bradley.edu/~campbell/demopix6.html>; (accessed Oct 2001).
- Campbell, D. J.; Freidinger, E. F.; Hastings, J. M.; Querns, M. K. *CHEM13 News*, in press.
- Frankel, F.; Whitesides, G. M. *On the Surface of Things: Images of the Extraordinary in Science*; Chronicle Books: San Francisco, 1997; pp 50–51.
- Bowden, N.; Carbeck, J.; Terfort, A.; Whitesides, George M. *Science* **1997**, *276*, 233–235.
- University of Wisconsin-Madison Materials Research Science and Engineering Center for Nanostructured Materials and Interfaces. Exploring Self-Assembly Processes Using Magnetic PDMS Tiles. <http://www.mrsec.wisc.edu/edetc/selfassembly/index.html>; (accessed Oct 2001).
- Bowden, N.; Choi, I. S.; Grzybowski, B. A.; Whitesides, G. M. *J. Am. Chem. Soc.* **1999**, *121*, 5373–5391.
- Huck, W. T. S.; Tien, J.; Whitesides, G. M. *J. Am. Chem. Soc.* **1998**, *120*, 8267–8268.
- Breen, T. L.; Tien, J.; Oliver, S. R. J.; Hadzic, T.; Whitesides, G. M. *Science* **1999**, *284*, 948–951.
- Tien, J.; Breen, T. L.; Whitesides, G. M. *J. Am. Chem. Soc.* **1998**, *120*, 12670–12671.
- LEGO is a trademark of the LEGO Group. Demonstrations and experiments using LEGO bricks can be found at <http://mrsec.wisc.edu/edetc/LEGO/index.html> (accessed Oct 2001). The part numbers for the LEGO magnet system are: 2609 – Magnet holder tile, 2 × 2 peg and 73092 – Magnet.
- The north- and south-pole designations in this paper are not absolute, but rather used to distinguish opposite orientations of the magnets.
- Cotton, F. A.; Wilkinson, G.; Gaus, P. L. *Basic Inorganic Chemistry*, 2nd ed.; John Wiley & Sons: New York, 1987; pp 175–176.