Autonomous Movement and Self-Assembly**

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Many complex systems—from swarming bacteria and schooling fish to transportation networks and capital markets—show a number of characteristics in common, among which are autonomous movement of the components of these systems, and interactions (which can be both attractive and repulsive) among these components.[1] We have begun a program to explore complexity by designing and fabricating/synthesizing components that both *move* and *interact* with one another, and then characterizing the patterns that emerge from groups of these components. As part of this program, we wish to develop entities capable of *autonomous* movement, and to explore the collective behaviors of these entities in motion. This paper describes the behavior of small (< 1 cm) hemicylindrical plates that have a small area of platinum on one surface and that float at the surface of an aqueous solution of hydrogen peroxide. These plates moved under the impulse of bubbles generated by the platinum-catalyzed decomposition of hydrogen peroxide ($2H_2O_{2(l)} \rightarrow O_{2(g)} + 2H_2O_{(l)}$).[2] The edges of these plates were also patterned to have hydrophobic and hydrophilic regions; capillary interactions between menisci at the hydrophobic edges attract the plates to one another. We have shown previously that capillary interactions can cause the assembly of periodic 2D and 3D structures in systems of particles with sizes ranging from 10 μm to several millimeters.[3]

Autonomous movement occurs in many animate systems and a surprising number of inanimate ones. Animate movement is normally due to the action of rotary and linear molecular motors—driven by the dissipation of ion gradients across membranes or by the hydrolysis of ATP.[4] Inanimate motion takes a wide variety of forms, with the simplest systems often taking advantage of gradients in concentration or temperature. Self-propulsion of camphor crystals placed on an air/water interface occurs by preferential dissolution of camphor from one of the sides of the crystal; this dissolution creates a gradient in surface tension of the air/water interface and induces motion.[5] Gels swollen with an organic solvent (such as ethanol or tetrahydrofuran) can move when slow injection of the solvent at one face of the gel locally reduces the surface tension.[6] Marangoni effects can generate motion in fluids or droplets under a variety of circumstances:[7] for example, a fluid film heated by a solid surface on one side and cooled by air on the other side spontaneously develops convection cells in which fluid motion transfers heat from the warmer to the cooler surface.[8] There are many other chemical systems that generate motion. A mercury droplet placed in proximity to a dissolving potassium dichromate crystal in water shows motion in the developing concentration gradient of the oxidant.[9] Pieces of sodium move on the surface of water while dissolving and reacting.[10] Tin clusters show complex motion on copper surfaces while alloying with the substrate.[11] These systems are all conceptually related and, although their components move, they do not offer a clear opportunity for the design of systems with motion and interactions that can be tailored. Most also suffer from the disadvantage that they consume or dissipate a material stored "on board" and are thus limited in the duration over which they can move and in the constancy of that motion.

We have designed a system in which the components move autonomously by ejecting small bubbles of gas formed by catalytic decomposition of a liquid. The fuel (or "food") required for motion is thus present in the environment and can, in principle, sustain motion indefinitely. Metallic platinum is an excellent catalyst for the decomposition of hydrogen peroxide into water and dioxygen. Under the conditions used in the experiments described herein, the action of this catalytic system is approximately constant over two hours, or five times the interval of time required to complete the experiments shown in the Figures. Plates floating in a container with a large amount (1 L) of the aqueous solution of hydrogen peroxide continued moving for several days, albeit with a slow decrease in velocity due to the depletion of H_2O_2 in solution; motion could be restored to its original level by replenishing the H_2O_2.

Self-propulsion. Self-propelling plates were fabricated from polydimethylsiloxane (PDMS) using rapid prototyping;[12] Figure 1 A shows the design. The plates were placed at the liquid/air interface of a 1–3% aqueous solution of H_2O_2 at room temperature. The evolution of gaseous O_2 began immediately and caused motion of the plates. These plates moved on the surface of H_2O_2 with velocities of up to 1–2 cm s^{-1} for several hours. This motion was reproducible for all plates in a group of 20 plates. The energy required for

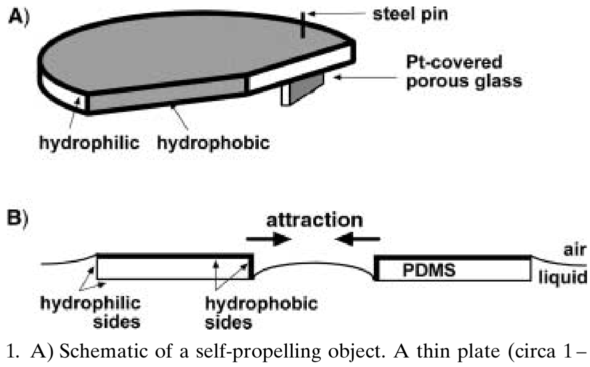

Figure 1. A) Schematic of a self-propelling object. A thin plate (circa 1–2 mm thick and 9 mm in diameter) was fabricated from PDMS in a desired shape, and specified faces were rendered hydrophilic by oxidation in a plasma formed in air. A 2 × 2 mm^2 piece of porous glass filter (covered with platinum by an electron beam evaporation) was mounted on the PDMS piece with a stainless steel pin. B) A diagram illustrating self-assembly by capillary interactions.

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movement comes from the recoil of the liquid as the bubbles burst.

Self-assembly. The hydrophobic sides of PDMS plates floating at a H_2O_2/air interface create negative menisci.[3a] When two such objects approach each other more closely than the capillary length (on the order of several millimeters), the menisci overlap and interact, and the objects are attracted to each other (Figure 1 B). The attraction is caused by the decrease in the total area of the H_2O_2/air interface, and the attractive force is proportional to the surface tension of that interface. Because the chemical reaction that is taking place on the plates does not significantly affect the surface tension of the liquid, surface tension driven self-assembly can take place in our system.

Chiral self-assembly. The hemicylindrical plates used in self-assembly (Figure 1 A) are chiral because the catalyst attached to a disk breaks both the left–right and top–bottom symmetries. A single plate rotates in the direction determined by its chirality (Figure 2). The direction of this rotation was reproducible for all plates (in a set of 20), but the frequency, the radius of curvature, and the position of the center of rotation differed slightly from plate to plate. This irregularity of motion of single plates is also visible prior to their self-assembly in pairs (Figure 3). We have designed these plates so they could assemble in pairs of two configurations: a) Plates of the opposite chirality can assemble into heterochiral dimers (Figure 3 A); b) plates of the same chirality can assemble into homochiral dimers (Figure 3 B). The heterochiral dimer moves unidirectionally, in contrast to the rotational motion of individual plates. The average velocity of this dimer is 2–3 times higher than that of the individual plate (Figure 3 A). The homochiral dimer rotates in the same direction as its individual plates, although its rotation is more regular than that of the isolated plates (Figure 3 B).

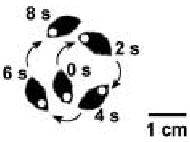

Figure 2. Overlaid photographic images that show catalytic self-propulsion of a single plate of the type shown schematically in Figure 1. On this and the following Figures, white dots were added onto the photographs to indicate the catalyst-bearing tips of the plates.

Figure 3 B also shows that motion ensures that plates assemble into the most stable configuration. At $t = 38$ s two plates assemble into a metastable configuration that persists until $t = 52$ s (not shown) and then rearranges into the stable configuration (with maximum hydrophobic–hydrophobic contact) at $t = 54$ s. We base our assignment of the relative stability of the two configurations on the fact that we have never observed the reverse rearrangement to occur.

We also wished to establish whether interactions of larger number of plates could lead to a different type of collective behavior. When ten plates (five of each chirality) were allowed to float on the surface of hydrogen peroxide, four pairs assembled in approximately 20 min (Figure 4) with no pronounced selectivity in assembly for homochiral versus heterochiral dimers (four experiments). The last pair did not assemble in the next 20 minutes, and we attribute this fact to the decrease in the rate of assembly as the surface density of single plates decreased.[13] These results indicate that inter-

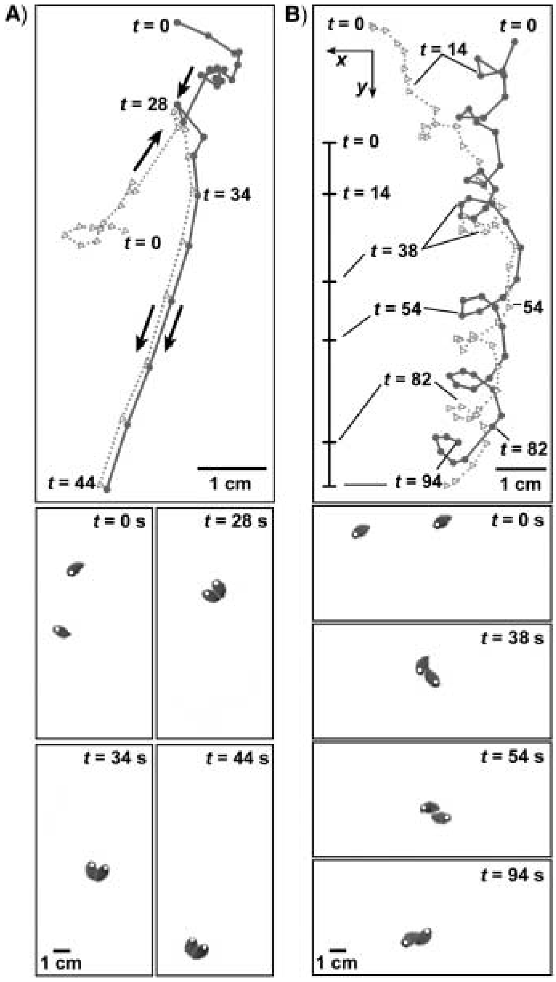

Figure 3. Graphs and images that illustrate motion and self-assembly of self-propelling plates (shown in Figure 1 A) in 3 % H_2O_2. On graphs, the symbols indicate the position of the piece at two-second intervals. A) Two plates of opposite chirality assemble into a dimer that moves translationally. On the graph, the symbols correspond to the position of the tip of the plate that does not bear the catalyst. B) Two plates of same chirality assemble into a dimer that moves rotationally. On the graph, the symbols correspond to the position of the catalyst-bearing tip of the plate. To deconvolute the rotational motion, we have transformed the vertical y-axis [cm] of the plot to a new y' axis that shows both the position on the y coordinate and time t [s] using the relation $y' = y + 0.1\,t$. This stretching of the y-coordinate with time allows us to show the last three cycles of the rotational motion of the aggregate; in fact, these three cycles of rotation occur around a center that is approximately fixed. Bars crossing the vertical line correspond to the position of a stationary point at $t = 0$, 14, 38, 54, 82, and 94 s.

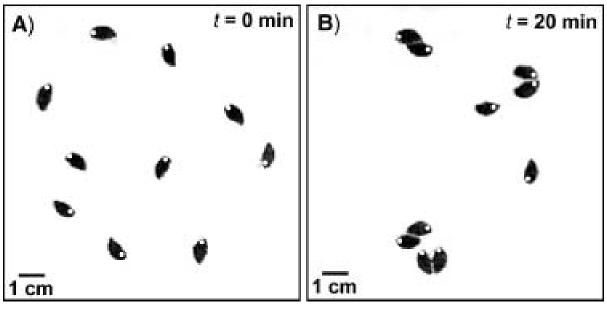

Figure 4. Photographs showing self-assembly of 10 plates (5 of each chirality). Initially (A), isolated plates were randomly distributed. In approximately 20 minutes (B), 4 pairs assembled into dimers.

actions of five pairs of plates do not lead to an additional level of complexity; larger numbers of plates, or plates designed to have multiple interactions, may be required before the system shows unexpected ("emergent") behavior.[14]

This paper is the first step towards our goal of creating artificial complex systems composed of large numbers of components that move autonomously, and that self-assemble. To achieve the goal, we must design a system in which we can control both motion and self-assembly, and must make components small enough so that interactions of large numbers of them can be studied. This paper describes the first artificial system of autonomously moving and self-assembling components in which the interactions among the components can be controlled through their design. This system has three advantages: a) The plates can be designed to move at a controlled velocity in different environments with a range of concentrations of the fuel, because the rate of decomposition can be controlled by controlling the amount and the activity of the catalyst; b) The plates can be made to assemble into aggregates of different stability because the strength of capillary interactions among the plates can be controlled through the thickness of the plates, their density, and the hydrophobicity of their surfaces; c) The energy required for motion is derived from the environment rather than from limited supply of fuel stored inside the plates, and the plates can therefore be made small yet still move over long periods of time. The disadvantage of the system is that all the processes take place at a fluid/air interface and are confined to two dimensions. If the system were transferred into the bulk of the solution, bubbles formed by the decomposition of the solution would affect the buoyancy of the plates and would make their motion more complicated and less predictable.

Self-assembly of autonomously moving components may find applications in the bottom-up fabrication of small functional systems. In addition, it suggests applications as a new type of self-assembly—one in which the products of self-assembly sort themselves. For example, our method of self-assembly forms heterochiral dimers with a statistically expected 50% yield, but there is a difference in the behavior of the dimers: Both the single plates and homochiral dimers rotate approximately in place, while the heterochiral dimers move in straight lines. Even though the self-assembly proceeds with a 50% yield, the system is one in which the heterochiral and homochiral dimers can separate themselves because the heterochiral dimer can swim out of the mixture of plates and dimers.

In examining emergence in a system, an important question is "How many interacting components are required in order for the system to show behavior that is not predicted from the properties of the components?" In this system, a new property (motion in a straight line), not present in the separate components, appears upon assembly of just two plates into a heterochiral dimer. We believe that assemblies of a moderate number of components—tens or hundreds—may show substantially more complex behaviors, but still be amenable to controlled experimentation. Such systems could find technological applications, and could help to understand behavior of other complex systems characterized by large number of autonomously moving, interacting components (for example schooling fish and swarming bacteria).

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[2] The H_2O_2–Pt system is not the only combination of energy source and catalyst that generates motion. Particles bearing dispersion of MnO_2 in cured PDMS also serve as catalyst for the decomposition of H_2O_2. Enzymes (catalase and carbonic anhydrase) embedded into a gel catalyze decomposition (of H_2O_2 into H_2O and O_2 and of H_2CO_3 into H_2O and CO_2, respectively) and lead to motion. The H_2O_2/Pt system was the most reproducible of these alternatives.

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[13] This lack of assembly is not due to the loss of hydrophobicity of PDMS in H_2O_2. Floating on the surface of 3% H_2O_2 for 2 h did not affect the propensity of the plates to assemble—20 plates out of the batch of 20 formed stable dimers with each other.

[14] We use the word "emergence", although it is not clear yet whether emergence is a fundamentally new concept, or a word with which to describe systems that are not yet understood but can be understood in principle.