Macroscopic Synthesis of Self-Assembled Dissipative Structures†

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This paper describes the preparation and manipulation of several coexisting, dynamically self-assembled aggregates of millimeter-sized, magnetized disks floating at a liquid−air interface and spinning under the influence of a rotating external magnetic field. Local minima in the in-plane energy profile of these disks are created by positioning ferromagnetic needles above the plane of the interface; these needles concentrate the magnetic field locally in that plane. Spinning disks assemble in the local minima, and the positions and geometries of their aggregates can be manipulated spatially by changing the positions of the needles. Fragmentation and fusion of aggregates in response to changes in the magnetic fields are described.

Self-assembly[1−7] in dynamic systems[8−10]—that is, in systems that develop order only when dissipating energy—can lead to multiple final structures; the structure(s) reached are determined by energy fluxes through the system and by the history of its evolution. Dependence of structure on flux and history implies that the products of dynamic self-assembly are, in principle, sensitive to their internal configuration and to external conditions and that dynamic systems are plausible precursors to *adaptive matter*[11,12]—that is, matter whose structure and properties change autonomously in response to external stimuli. This dependence also suggests that the spatio-temporal nature and sequence of external stimuli might make it possible to interconvert structures and that "synthetic" methodologies, analogous to those used in molecular sciences, might be developed for dynamic systems at mesoscopic and macroscopic length scales. These methodologies would enable the preparation of assemblies by the "reaction" of precursor assemblies.

We have recently described a dynamic, self-assembling system[13,14] of millimeter-sized, magnetized disks floating on a liquid−air interface and spinning under the influence of a rotating external magnetic field. The rotating magnetic field produces an average confining potential that acts on all disks and results in a force on them directed toward the axis of rotation of the magnet. The rotation of the disks in the fluid gives rise to repulsive, hydrodynamic interactions between them. As the result of the interplay between the magnetic and the hydrodynamic forces, the disks organize into regular structures. Here, we show that local modifications of the external magnetic field accomplished by positioning ferromagnetic needles ("field concentrators") in the region just above the liquid/air interface allow preparation of groups of locally ordered, coexisting aggregates of spinning disks. The morphologies of these aggregates change in response to the changes in the local perturbations of the magnetic field and "react" in processes loosely analogous to atomic/molecular reactions—that is, they fragment or fuse, forming other aggregates. We suggest that this system is a primitive macroscopic realization of a form of adaptive matter, and one having the useful experimental characteristic that many of the characteristics of the interacting components can be controlled.

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Experimental Procedure

Figure 1a outlines the experiment schematically. Disks (∼1 mm in diameter, ∼200 μm thick, $\rho \sim 1.2$ g/cm^3) were made of a commercial epoxy doped with 15 wt % magnetite powder, using a microtransfer molding technique described elsewhere.[15] The disks were placed at the interface between air and a 3:1 by volume mixture of ethylene glycol and water.[16] The disks were completely immersed in the liquid except for their top surface; this geometry minimized capillary interactions between them.[17] Although the disks were slightly more dense than the liquid, they were held at the interface by surface tension. A permanent bar magnet of dimensions $L \sim 5.6$ cm $\times$ $W \sim 4$ cm $\times$ $T \sim 1$ cm was placed under the dish, ∼3 cm below the liquid−air interface supporting the disks, and rotated with angular velocity $\omega \sim 500$ rpm. The magnet was magnetized along its longest dimension and had magnetization $M \sim 1000$ G/cm^3.

Forces Acting in the System: (i) Magnetic Interactions. All disks experienced a magnetic force $F_{m,r}$ that acted in the plane of the interface and was proportional to the gradient of magnetic induction produced by the rotating permanent magnet at the location (r, θ, z) of the disk. Because, as we verified experimentally, the positions of the disks did not change substantially during one revolution of the magnet, $F_{m,r}$ can be well approximated as centrosymmetric (around the axis of rotation of the external magnet). The magnitude of $F_{m,r}$ is proportional to the derivative of the time average (over one revolution of the magnet) of the radial component of magnetic induction along the radial direction r (pointing from the axis of rotation of the magnet toward the disk): $F_{m,r} \propto \partial\langle B_r(r,\theta,z)\rangle/\partial r$. In the following, we qualitatively describe the magnetic field in the plane of the interface supporting the disks. The detailed calculation of the field profile for the axially symmetrical case (Figure 1b, left) using the current-sheet method is described elsewhere;[13] the calculation for the arrangement with the field concentrator above the rotating magnet (Figure 1b, right) is too complex for us to carry out, and the curves are schematic.

The left photograph in Figure 1b shows the field lines above the rotating permanent magnet visualized using iron filings suspended in a viscous polymer, poly(dimethylsiloxane); the horizontal dotted line corresponds to location of the plane of the liquid/air interface. Because the iron filings follow the flux

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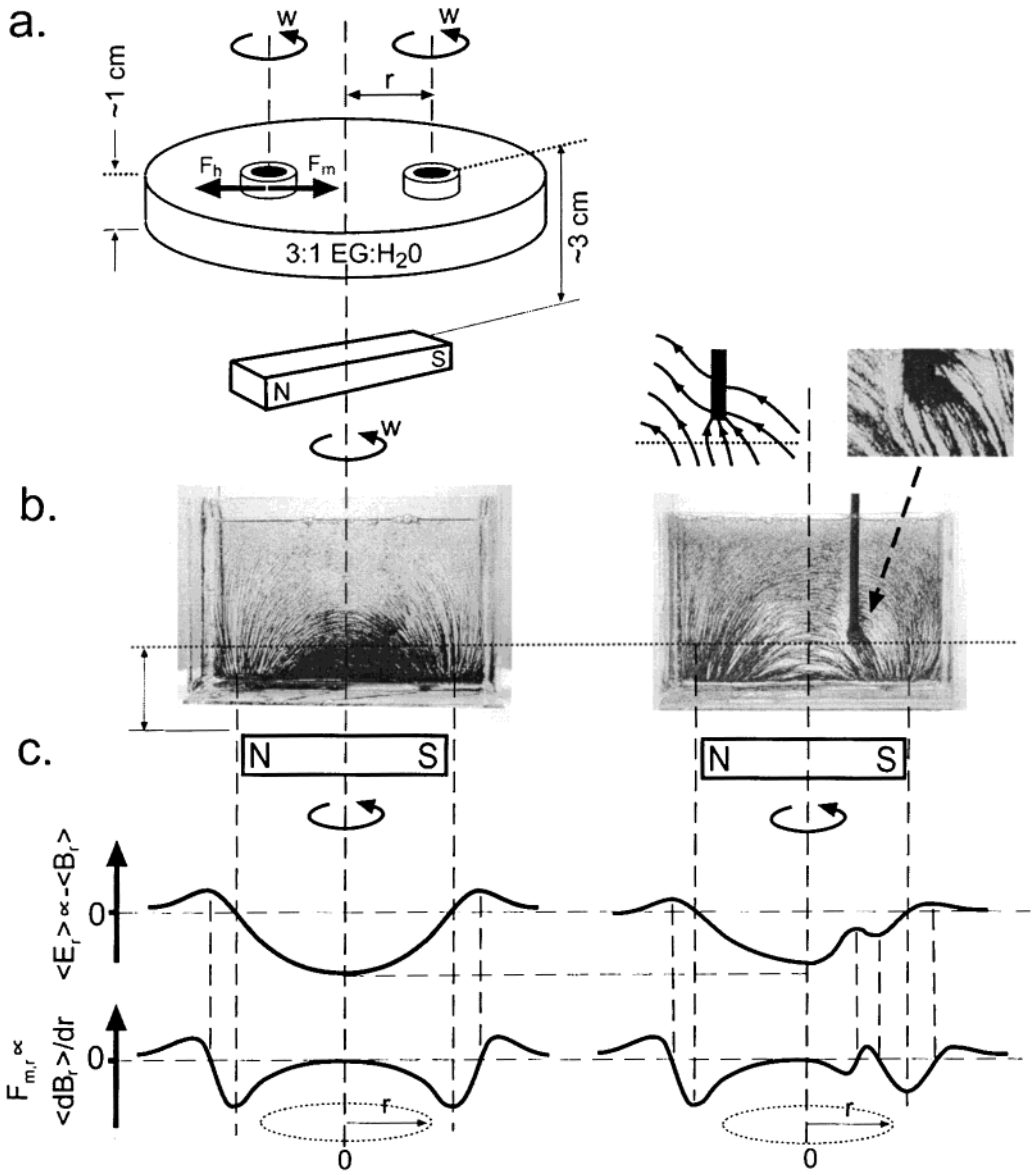

Figure 1. (a) is a scheme of experimental arrangement. The pictures in (b) show the field-lines (i) above a rotating bar magnet (left picture) and (ii) in a system composed of a rotating bar magnet and a magnetic flux concentrator positioned ~2 cm from the axis of rotation of the magnet (right picture). The insets in the right picture describe the field lines near the tip of the concentrator. The dotted line corresponds to the plane on the liquid/air interface in the experimental system. The graphs in (c) have the profiles of (i) the average radial component of the magnetic induction (proportional to the energy of the magnetic field; top row) and (ii) the radial derivative of the average radial component of magnetic induction in the plane of the interface (middle row). The graphs in the left column correspond to the left picture in (b), and those in the right column, to the right picture.

lines, and because their density (i.e., the number of field-lines per unit area) is linearly proportional to the flux density, the average of the scalar value of the radial component of the magnetic induction $\langle B_r \rangle$ at any location in the plane of the interface can be estimated from the horizontal projection of a field line at this location and from the density of lines around this point. For example, the field lines around the axis of rotation of the magnet are horizontal, and their density is higher than at any other position within the interface. The point of intersection of the axis of rotation of the magnet and the plane of the interface, therefore, corresponds to the highest value of $\langle B_r \rangle$. Analogous analyses performed at other loci allow construction of a qualitative profile of $\langle B_r \rangle$ within the interface (Figure 1c, upper graph). The dependence of the magnetic force $F_{m,r}$ on r is estimated from the changes in $\langle B_r \rangle$ along the direction of r, that is, from the slope of $\langle B_r \rangle$. The lower graph in Figure 1c shows that the magnetic force is attractive within a circle of radius approximately equal to half the length of the magnet and is repulsive otherwise. Finally, the profile of energy of a magnetized disk subject to the centosymmetric magnetic force $F_{m,r}$ is obtained by defining the zero of energy at $r = \infty$ and calculating $\langle E_r(r) \rangle = \int_r^\infty F_{m,r}(r)dr$. Since $F_{m,r} \propto \partial \langle B_r \rangle / \partial r$, it follows that $\langle E_r \rangle \propto -\langle B_r \rangle$ so that a qualitative energy profile is obtained directly from that of $\langle B_r \rangle$ by inverting it with respect to the ordinate axis; the field imposes a central confining potential on all disks and attracts them toward the axis of rotation of the magnet.

When the magnetic field is modified by placing field concentrators (here, ferromagnetic steel needles, 1−3 mm in diameter) above the plane of the interface (with separations ~1−10 mm), the magnetic forces acting on the disks in the plane of the interface change. The right picture in Figure 1b illustrates the deflection of the field lines of a rotating bar magnet toward the tip of the concentrator. This deflection changes the horizontal component of magnetic induction in the vicinity of the concentrators (Figure 1c, upper graph) and thus creates a field

gradient (proportional to the magnetic force) in the plane of the interface on which the disks float (lower graph). The corresponding energy profile shows that a local minimum of energy is created below the concentrator, near its axis (but *not* directly on the axis itself). Magnetized disks can form stable aggregates at the locations of the interface corresponding to the energy minima below the concentrators.

(ii) Hydrodynamic Interactions. The induced magnetic moments of the disks interacted with the rotating magnetic field, and the disks spun around their axes with angular frequency ω equal to that of the external magnet. The fluid motion associated with the spinning of the disks gave rise to repulsive vortex−vortex interactions between them. We have previously suggested[14] that the origin of these repulsions can be explained using ideas from low Reynolds number hydrodynamics. According to our analysis (described in full elsewhere[10]), the hydrodynamic repulsion $\underline{F}_{ij}^{j}$ exerted by a disk of radius a_j on a disk of radius a_i depends on the radii of the disks, the distance d_{ij} between their centers, the rotational speed ω, and the density of the fluid ρ. The hydrodynamic force is proportional to $\rho\omega^2 a_j^5 a_i^2/d_{ij}^3$ and acts along the direction of d_{ij} and away from disk j.

Preparation of Coexisting, Locally Structured Aggregates. We performed two experiments in which we studied the self-assembly of disks in the presence of external perturbations to the magnetic field induced by ferromagnetic needles. In the first experiment (one involving disks of equal size), the magnitudes of hydrodynamic forces between the disks were smaller than the magnitudes of the magnetic forces due to the local perturbation of the field of the rotating magnet by the needles. In the second (one involving disks of two different sizes), the hydrodynamic forces were comparable to the magnetic forces. These two regimes corresponded to different modes of self-assembly.

(i) Disks of Equal Size. Figure 2 shows the fragmentation of an aggregate composed of 37 disks (1.27 mm in diameter) into seven smaller, stable aggregates in response to changes in the magnetic field. A polystyrene plate supported seven needles that were positioned at the vertices and the center of a hexagonal pattern; the distance between adjacent needles was ∼2 cm. This plate was positioned above and parallel to the plane of the interface and was attached to a translation stage, so that the position of the tips of the concentrators above the interface could be adjusted (Figure 2a). Initially, when the ends of the needles were far from the interface ($h \sim 30$ mm), the average magnetic field of the rotating magnet in the plane of the interface was essentially unaffected by them. The disks then organized into one large aggregate with approximately hexagonal ordering (Figure 2b). When the concentrators were brought closer to the interface ($h \sim 5$ mm), shallow minima in energy appeared. The disks localized in these minima in the form of orderless aggregates (Figure 2c); these aggregates fluctuated in shape and occasionally exchanged disks with one another (Figure 2c). When the tips of the concentrators were close to the interface ($h \sim 2$ mm; Figure 2d), the minima in energy were deep enough to prevent exchange of disks, and the aggregates that formed in these minima were well-ordered. The aggregates precessed around the loci corresponding to the minima of energy in each of the energy "wells" (slightly off the axis of the field concentrators, cf. Figure 1c).

The ordering in some of these aggregates was sometimes different from that observed for the same number of disks in the more shallow magnetic wells formed by the rotating external magnet in the absence of the field concentrators. Thus, for example, the structure in the upper right corner of Figure 2d composed of nine disks (in which eight disks form a shell around a central disk), was different from the structure formed by nine

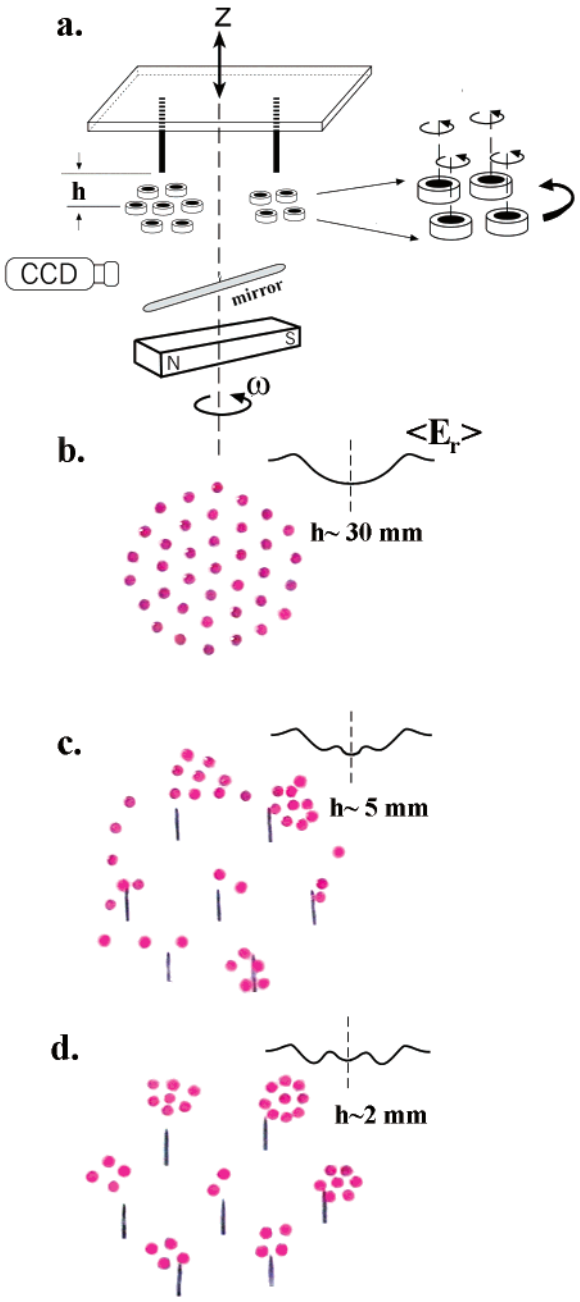

Figure 2. (a) outlines the experimental arrangement used to prepare aggregates of spinning disks on one liquid/air interface by dimpling the magnetic field using ferromagnetic needles as field concentrators. The needles were attached to a polystyrene plate; the plate was connected to a translation stage that allowed its elevation above the level of the interface to be adjusted. To visualize the formation of the aggregates below the field concentrators, a tilted mirror was positioned below the dish. This mirror gave an image of these aggregates as they formed; the image was recorded by a CCD camera. Within each small aggregate, all disks were spinning around their axes ($\omega \sim 500$ rpm), and each aggregate precessesed slowly ($\Omega \sim 10$ rpm) around an axis near (but not exactly coinciding with) that of the field concentrator. The pictures in (b)−(d) illustrate fragmentation of an aggregate composed of 37 disks (1.27 mm in diameter), into seven smaller aggregates by an array of seven needles. The pictures in the right column give qualitative profiles of the energy of magnetic field at each stage of the fragmentation; h is the distance between the tips of the concentrators and the plane of the interface. The aggregates in (c) were unstable in shape and number of disks; those in (d) were stable.

disks in the presence of the unmodified magnetic field of the rotating magnet (i.e., two disks in the center and seven disks in the shell around them). The aggregate formed by the field concentrator was also more compact than that in its absence, with a difference in radius of approximately 30%. The structures observed under the influence of the field concentrators reflect the effects of tight magnetic confinement of the disks by the deep local minima, and their existence was predicted in computer simulations for steep magnetic potentials.[18]

(ii) Disks of Different Sizes. In the experiments with 1.27 mm disks, the number of field concentrators specified the number of aggregates resulting from fragmentation, but the numbers of disks within each aggregate varied. We wished to be able to generate systems that would form a specified number of small aggregates with at least partly defined internal structures under the influence of the field concentrators. When we used larger disks, with one large disk per magnetic flux concentrator (and thus, energy minimum), the aggregates that formed spontaneously had at most one large disk per energy minimum. Figure 3 illustrates fragmentation of an aggregate composed of 37 small (O.D. 1.27 mm) and seven large disks (O.D. 2.42 mm) into seven aggregates. In the absence of the field concentrators the assembly was unstable (Figure 3a). Because the small disks at the periphery of the aggregate were moving near the edge of the rotating magnet, they experienced an inhomogeneous magnetic field and were often off-resonance with the field so that they occasionally stopped spinning. The erratic motions of these disks prevented the aggregate from assuming a stable conformation. At small perturbations to the average magnetic field of the rotating magnet ($h \sim 10$ mm, Figure 3b), the local energy minima were broad and shallow, and disks exchanged among them. Under these circumstances, up to two large disks could occupy one minimum. When the magnetic confinement was increased by lowering the concentrators, two large disks could no longer coexist within one minimum. The large hydrodynamic repulsions between the 2.42 mm disks (calculated to be more than 2 orders of magnitude larger than repulsions between two 1.27 mm disks spinning with the same rotational speed[14]) prohibited placing two such disks at short separations within a highly localized energy minimum. As the result, the large disks distributed themselves with one disk under each concentrator. At $h \sim 5$ mm (Figure 3c), the small disks still switched between the local minima, but at $h \sim 2$ mm (Figure 3d) the configurations were frozen—each concentrator had exactly one large disk under it, and a number (up to 12) of small disks that was different from well to well; these small disks no longer exchanged between the wells. The central field concentrator confined only a large disk but no small disks: the flows created in the liquid by the surrounding, precessing aggregates facilitated transfer of small disks away from the central, shallow minimum.

Manipulation of the Aggregates: Macroscopic "Synthesis". The aggregates in which the large central disk organizes small disks into concentric shells precessing around it are reminiscent of the early, classical models of an atom. In fact, we have previously suggested[14] that such aggregates can be regarded as macroscopic models of these so-called "classical artificial atoms"[19,20]—that is, as models of microscopic systems composed of finite numbers of interacting classical particles confined by an external field and repelling one another. In the previous section, we described how spatial variations of the external magnetic field induce self-assembly of such macroscopic, classical "atoms"; in this section, we show how temporal changes in the magnetic field caused by removing magnetic

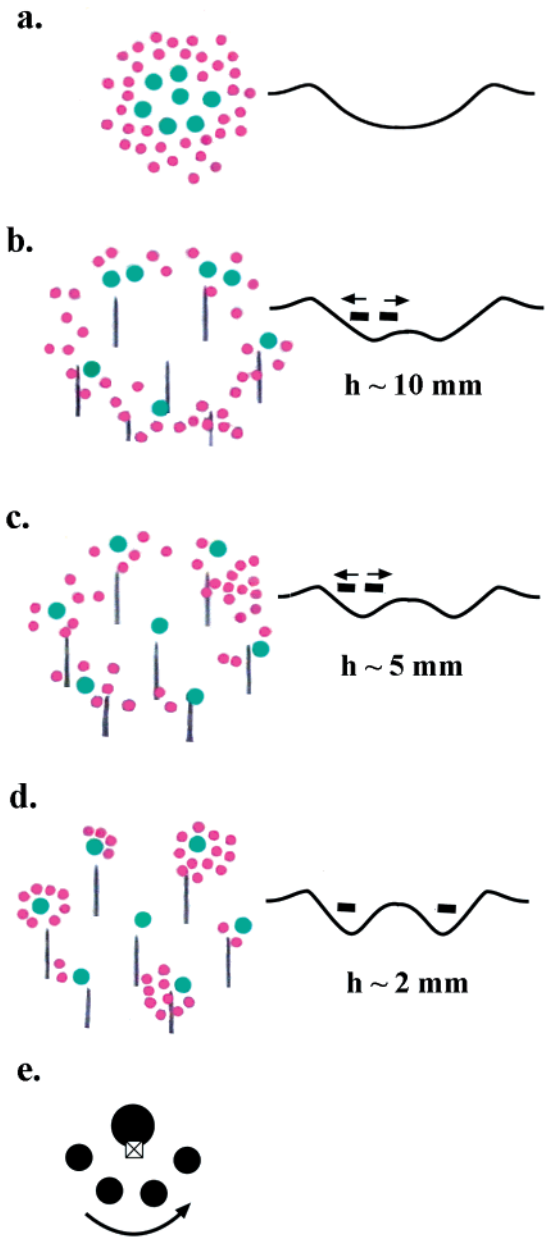

Figure 3. (a)−(d) illustrates the fragmentation of an unstable assembly of 37 small (O.D. 1.27 mm) and seven large (O.D. 2.42 mm) disks into six stable aggregates, each composed of one large disk and varying numbers of smaller disks as the depth of the wells induced by the field concentrators increased. The pictures in the right column give qualitative profiles of the energy of magnetic field (along a line joining two adjacent field concentrators) at each stage of the fragmentation. As the concentrators were brought closer to the interface, the energy minima became deeper and narrower; strong hydrodynamic repulsions between the large disks prevented more than one of them from occupying the same minimum. The schematic drawing in (d) illustrates the precession of a typical aggregate around the local minimum of energy (indicated by a marker).

field concentrators cause the "atoms" to evolve into a larger, "molecular" aggregate. We suggest that this process can be considered a kind of "synthesis"—that is, a "reaction" involving the combination of two classical "atoms" into a classical "molecule".

The top picture in Figure 4 shows two "atoms" that self-assembled in two regions of the interface corresponding to the minima of the energy of magnetic field; these minima were created, as before, using field concentrators. Because of large hydrodynamic repulsions between large spinning disks in a

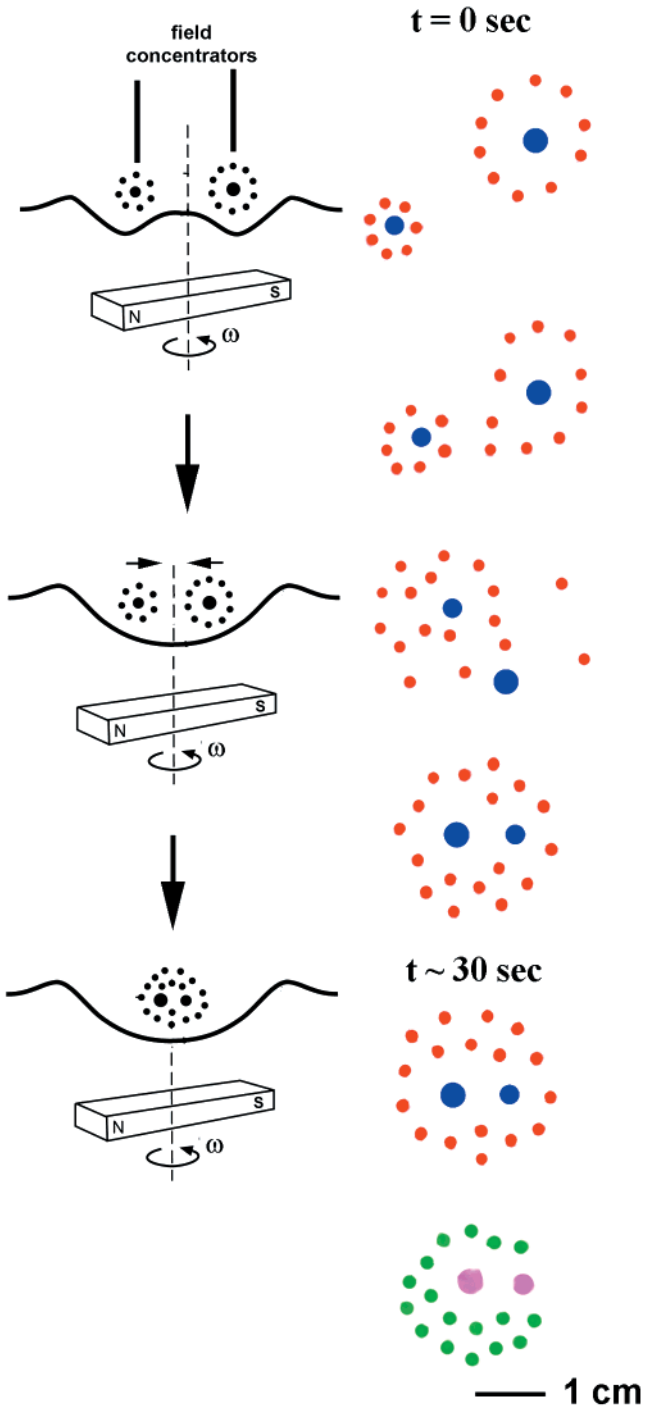

Figure 4. Fusion of two macroscopic "artificial atoms" into an "artificial molecule". The smaller "atom" is composed of one disk 2.08 mm in diameter (blue) and seven disks 1.27 mm in diameter (red); the larger atom has one 2.42 mm disk and ten 1.27 mm disks. The "atoms" are initially prepared in two separate energy minima. When the field concentrators are removed, both assemblies are released from their local minima and attracted toward the center of the rotating magnetic field, around which they fuse and form (after ~30 s) a larger, stable aggregate ("molecule"), in which small disks form shells around the centrally positioned large disks. When a "molecule" is formed from random initial configurations of the disks, it sometimes evolves into an open-shell structure (pink-and-green aggregate) never obtained from the fusion of two atoms.

single local potential, each of the large disks evolved into a different minimum, and organized small disks around it. The "atoms" generated by this procedure were stable and could be moved across the interface by moving the concentrators. When the concentrators were removed, the minima in the energy profile disappeared, and both "atoms" moved toward the axis of rotation of the magnet: there, they fused into a larger aggregate with two large disks in its center—a macroscopic "molecule". The small disks in this "molecule" organized into shells around the large disks. For a given total number of disks, the inner shell always had the same number of disks. For instance, in the "molecule" shown in the lowest picture in Figure 4, there were always 12 disks in the first, closed shell, while the remaining five disks were distributed between two clusters on the opposite sides of the axis joining the centers of the large disk (here, one cluster had four disks, and the other had one disk); the numbers of disks in these outer clusters differed between experiments.

The synthesis of the "molecule" from two "atoms" led reproducibly to the closed-shell morphology shown in Figure 4. In contrast, when the molecule was formed from random initial configurations of the same numbers of disks, it sometimes had the first shell of the small disks open (the pink-and-green structure in Figure 4). Such open-shell structures formed when the largest (2.42 mm) disk reached the position around the axis of rotation of the magnet before the 2.08 mm disk and had enough time to organize several 1.27 mm disks around it. The incoming 2.08 mm disk experienced the hydrodynamic repulsion of an already formed structure, and because it was unable to perturb it, it was trapped in its outer shell. When the same assembly was prepared from "atoms", the 2.08 mm disk had small disks around it at all times, so when it "collided" with the 2.42 mm disk (and small disks around it), the small disks on both "atoms" were perturbed; both large disks could penetrate into the center and subsequently organized small disks around them.

This result illustrates that a "synthetic" approach to dynamic self-assembly can direct the evolution of a system into well-defined structures. The pathway involving preparation of the initial self-assembled structures ("reactants"), and their subsequent evolution into a larger aggregate ("product"), yielded different products than those resulting from the assembly of initially disordered disks.

The success of the "synthetic" approach depends on the ability to first prepare the system in the desired "reactant" states (e.g., two "atoms", and not a smaller "molecule" and several small disks). In this regard, the experiments in which larger aggregates were fragmented into smaller ones by introducing dimples in the magnetic field with the field concentrators introduced an important concept: that is, the importance of the relative magnitudes of the external disturbances and the internal forces acting in the self-assembling system. We suggest, as a general *heuristic* principle, that the best control over the morphologies of the self-assembled "reactant" assemblies is achieved if the magnitude of the external perturbation is comparable to that of a dominant internal interaction. In fragmentation of aggregates of disks of different sizes (Figure 3), the magnitude of the magnetic confinement produced by the field concentrators matched that of the hydrodynamic repulsions between the large disks (dominant hydrodynamic interaction), and the system evolved into "atoms" (and not "molecules" or aggregates of only small disks). Had the external confinement been stronger, more than one large disk would have been able to fit into one energy minimum (as during fragmentation of aggregates of small disks, where the local minima accommodated several disks); had it been weaker, the large disks would have escaped from them and the system would have been unstable.

We believe that this system and others analogous to it can contribute to research in three areas: (i) In self-assembly, the system can be useful as a model for theoretical studies of evolution and flux-structure relations in self-organizing systems. The method described here to cause the sequential reaction of self-assembled structures by controlling energy fluxes through them can be extended to systems based on types of interactions other than magnetic and hydrodynamic, and thus extend the scope of dynamic self-assembly. (ii) In condensed matter physics, this system provides a macroscopic model for interactions between classical artificial atoms. This analogy is validated by quantitative similarity between the interactions that govern the physics of the spinning disks (r^{-n} pairwise repulsions) and those in microscopic systems of classically behaving particles. (iii) In engineering, the aggregates of rotating magnetized objects might be used as small machines. We are currently studying systems of gear-shaped plates in this context. The use of field concentrators allows us to adjust the local magnetic field conveniently, and thus to manipulate the gears in the plane of the liquid/air interface.

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(16) Kinematic viscosity of the mixture affected the stability of the aggregates. In liquids of low viscosities ($\nu < \sim$3 cp), the flows created by spinning disks were often turbulent, and the self-assembled aggregates were unstable. If the viscosity was too high ($\nu > \sim$ 50 cp), the magnetic torque was too small to spin the disks. Most stable structures were observed in liquids of intermediate kinematic viscosities, such as the 3:1 mixture of EG and water ($\nu < \sim$10 cp).

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