

Complexity and dynamic self-assembly

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Abstract

Physico-chemical complex systems are composed of many non-linearly interacting components, operate away from thermodynamic equilibrium, are adaptive to their environment, and often organize into patterns. Understanding the principles that govern such systems might lead to better understanding of life and to new types of technological applications. This contribution describes a bottom-up approach to studying complex systems, in which they are “synthesized” from smaller subunits and properly tailored interactions; the “synthesis” is guided by a set of heuristic design rules. This approach was used to develop a class of dissipative complex systems based on magnetic and hydrodynamic interactions. Some of the designed ensembles were the basis of successful microfluidic and mechanical devices.

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1. Introduction

Complexity (Nicolis and Prigogine, 1998, 1977; Whitesides and Ismagilov, 1999) is a concept that is intuitively obvious, but not easily precisely defined. One says, familiarly, that a system is complex if it shows complicated behavior or characteristics, and if it is difficult to understand or predict its behavior from parameters that can be observed. Although being complicated is a prerequisite for being complex, these two terms are not equivalent. A molecular mechanics calculation might be computationally complicated, but it is predictable, and its outcomes are congruent with chemical intuition. Complex phenomena, on the other hand, are usually counter-intuitive and surprising. It is unexpected, for example, that an assembly of neurons in the brain gives rise to consciousness. Or that putting together 57 genes and 59 proteins creates intricate, life-like machinery known as a T7 virus.

The world is populated by complex systems (CS), and many of them are vitally important: life or the cell is the prime example; weather, economic systems, and large networks (chemical reactions, computers, information systems, energy distribution grids, manufacturing processes) are other examples. Learning how to think about these systems,

and how best to predict and/or control their behavior, has now become a central and ubiquitous problem in science and engineering.

There are two approaches to study complex systems: top-down and bottom-up. In the former, one analyzes a known CS and strives to derive a simple mathematical model that would adequately describe its behavior. This reductionist strategy has been successful in explaining the principles of several important classes of complex systems (e.g., Benard convection (Koschmider, 1993)) reaction–diffusion (Jakubith et al., 1990; Turner, 1985; Kirscher et al., 2001), swarming of motile organisms (Shimoyama et al., 1996; Bonabeau et al., 2000; Shapiro, 1998), networks (Strogatz, 2001)), but is inherently limited to existing experimental arrangements and cannot create new ones. In an alternative, bottom-up approach, one tries to create complex systems from simple components and design rules. To date, this approach has been applied mainly in theoretical constructs such as cellular automata (Adami, 1998) and Boolean networks (Kauffman, 1993; Gibson and Mjolsness, 2001). Our group strives to extend it into the experimental domain with the aim of developing a “synthetic” methodology that would allow rational design of physico-chemical complex systems (Whitesides and Grzybowski, 2002; Grzybowski et al., 2002b).

In this contribution, we first discuss the general principles that underlie our approach. We then illustrate how these principles were used in developing a class of simple,

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Table 1
Interactions and effects that can be used to synthesize new types of complex systems

Interaction	Attractive	Repulsive
Magnetic	Campbell and Grzybowski (2004); Martin et al. (2003); Giovanazzi et al. (2001)	Grzybowski and Whitesides, 2002; Martin et al. (2003); Yellen and Friedman (2003)
Electrostatic	Grzybowski et al. (2003); Mishchuk et al. (2001); Ye et al. (2003)	Grzybowski et al. (2003); Hoagland (1990); Yethiraj and van Blaaderen (2003)
Capillary/surface tension	Hosokawa et al. (1996); Lucassen, 1992; Nikolaides et al. (2002); Bowden et al. (1999)	Hosokawa et al. (1996); Lucassen (1992); Bowden et al. (1999)
Vortex/vortex	Grzybowski and Whitesides (2002); Grzybowski and Whitesides (2002a);	Grzybowski et al. (2000)
Steric shielding (polymer)		Lahiri et al. (1999); Shen et al. (1999)
Entropic: steric exclusion		Adams et al. (1998); Molle et al. (2003)
Hydrophobic	Hato (1996); Tanford (1978)	
Biospecific	Lahiri et al. (1999); Metallo et al. (2003); Tirrell et al. (2002)	
Hydrogen bonding	Braga et al. (1997); Grzybowski et al. (2000); Berl et al., 2000; Martin et al. (1998); Russel et al. (1997)	

non-equilibrium hydrodynamic systems that—under some circumstances—show complex behaviors.

2. Synthetic approach to complex systems

Despite the fact that complex systems come from so many different fields of science, those which are physical in nature (as opposed to purely theoretical constructs) share several commonalities: (i) they are composed of many components (discrete objects or continuous chemical species) that interact with one another by non-linear or multibody interactions; (ii) their components often spontaneously organize into patterns (spatial, temporal or both); (iii) they are adaptive to their environment so that their internal state can be changed by external stimuli; and (iv) they operate away from thermodynamic equilibrium. A particular complex system might have one or more of these properties. In addition, some complex systems exhibit sensitivity to initial conditions so that minor changes in controlling parameters result in dramatic changes in the system's state or can even make it chaotic.

To recreate at least some of these characteristics in the model systems we design, we formulated a set of simple, heuristic rules that guide our design.

2.1. Competitive interactions

We begin by identifying suitable phenomena and associated interactions. We require that the interactions within a system cannot all be of the same nature (i.e., all attractive or all repulsive) but rather have to “compete” with one another. If all the forces acting on the components

of the system were attractive, the components would simply aggregate into a stable, equilibrium structure; if they were repulsive, the system would disintegrate. Table 1 gives examples of forces/effects that we think suitable for our methodology.

2.2. Dissipation of energy

In order for the system to be responsive to external stimuli and potentially adaptive (Hanselka, 2001; Alstrom and Stassinopoulos, 1995) to its environment, the interactions of at least one type have to depend on the flux of energy through the system. In other words, it must be possible to change the magnitudes and sometimes even the nature of these interactions by changing the values of external parameters controlling the delivery of the energy to the system (e.g. frequency of impinging light, strength or frequency of external magnetic or electric fields, etc.). Although, in theory, a system could be conceived in which interactions between the components and the system's internal state (mode of organization) could be regulated by external fields without dissipation of energy, in practice, the externally delivered energy is always dissipated into microscopic degrees of freedom. Physically realizable dynamically self-organizing systems are thus dissipative.

2.3. Medium and length scale

Once the types of interactions are chosen for a particular system, we identify a proper environment and a length scale at which they can coexist. To illustrate this point, suppose a two-dimensional system is to be designed, in which particles attract by capillary forces (Bowden et al., 1999;

Grzybowski et al., 2001b) and repel one another by induced magnetic dipole–dipole interactions (Giovanazzi et al., 2001). An obvious choice of the medium/location is a liquid–liquid interface at which the menisci—and, consequently, the capillary forces—between the objects can be engineered. The capillary forces between floating objects are effective down to $\sim 100 \mu\text{m}$ (below that limit, gravity dominates capillarity); the magnetic dipole–dipole forces between superparamagnetic particles (ferromagnetic objects would be too dense to stay afloat at the interface) are negligible at length-scales $> 1 \text{ mm}$, but grow rapidly with decreasing size. Based on these characteristics, one would expect that the magneto-capillary CS can be built from objects down to couple of hundreds micrometers in diameter.

2.4. Increasing complexity

We design our systems in such a way that it is easy to increase their complexity by “hierarchically” building into them various new phenomena, new types of interactions or features. By doing so, we are able to study at which level of this “hierarchy” a system starts behaving in a complex/unpredictable way and what characteristics of the components are essential to give rise to such a behavior.

In the following, we describe how these principles were used to a class of systems based on competitive magnetic and hydrodynamic interactions. We will begin by describing a basic configuration (Grzybowski et al., 2000) in which identical components are confined by a centrosymmetric, magnetic potential, repel one another by vortex–vortex interactions and organize into two-dimensional, metastable lattices. We will then discuss how the forces acting within the system can be tailored in two and three dimensions, and how these modifications lead to unexpected behaviors such as symmetry breaking, chiral recognition and pattern replication. We will conclude by describing three applications originating from our model systems: a microfluidic mixer, a fluidic size-selective membrane and a fluidic machine.

3. Self-assembly of magnetic spinners: basic configuration

3.1. Experimental setup

Fig. 1a outlines the experiment. A permanent bar magnet (KIKA Labortechnik) of dimensions $5.6 \text{ cm} \times 4 \text{ cm} \times 1 \text{ cm}$ rotates with angular velocity ω (~ 200 – 1200 rpm) below a dish filled with a 3:1 by volume solution of ethylene glycol (EG) and water. The magnet is magnetized along its longest dimension and has magnetization $M \sim 1000 \text{ G/cm}^3$. The distance between the upper face of the magnet and the interface between the EG/H₂O mixture and air is $H \sim 30 \text{ mm}$, and the thickness of the EG/H₂O layer is $h \sim 1$ – 6 mm . The millimeter-sized polymeric disks (50 – $100 \mu\text{m}$ thick) are made of epoxy resin doped with 10–25% by weight

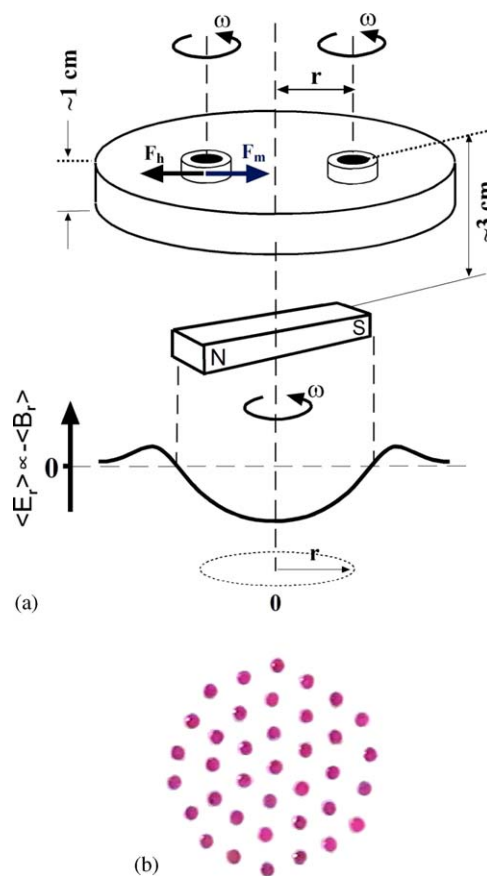


Fig. 1. (a) illustrates the simplest version of the experimental arrangement used in dynamic self-assembly of rotating magnetic disks. Magnetic force F_m attracts the disks towards the axis of rotation of the magnet, and the vortices these disks create in a surrounding liquid give rise to repulsive, pairwise hydrodynamic forces F_h between them. The graph below the scheme has the profile of the average radial component of the magnetic induction—proportional to the energy of the magnetic field—in the plane of the interface. The photograph in (b) shows an aggregate formed by 37 rotating disks 1.57 mm in diameter. Once organized, this dissipative structure slowly precesses around its center, and is stable for days.

magnetite, and are fabricated using a micro transfer molding technique described previously (Xia and Whitesides, 1998).

3.2. Forces acting within plane of the interface

Under the influence of the magnetic field produced by the rotating magnet, all of the disks floating on the two interfaces experience a centrosymmetric force F_m directed towards the axis of rotation of the magnet. With the magnet used in our experiments, and for $H \sim 3$ – 4 cm , this magnetic force is a slowly varying, approximately linear, function of position within an interface: $F_m = -c_m |r| \hat{r}$, where c_m is a constant (Grzybowski et al., 2001a).

Because the magnetic moments of the disks interact with the magnetic moment of the external rotating magnet, the disks spin around their axes at an angular velocity ω equal to that of the magnet. The fluid motion associated with spinning

results in repulsive hydrodynamic interactions F_h between the disks. The origin of these repulsions can be explained using ideas from low (but not zero)-Reynolds-number hydrodynamics (Grzybowski et al., 2000). According to this analysis, the hydrodynamic repulsion F_h^{ij} 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 : $F_h^{ij} \propto \rho \omega^2 a_j^5 a_i^2 / d_{ij}^3$. The force on disk i acts along the direction of d_{ij} and away from disk j . The interplay between attractive and repulsive interactions between the disks floating on the same interface leads to formation of patterns (Fig. 1b), in which spacing between the disks depends—other parameters held constant—on their rotational speed.

3.3. Length scale

The major limitation to down-scaling our system is the rapid increase of the magnitude of the interactions between magnetic dipoles induced in the rotating particles by the external field with the decreasing size of these particles (Grzybowski and Whitesides, 2002). The induced dipole–dipole forces are attractive and scale as d_{ij}^{-4} . They dominate the hydrodynamic repulsions when the size of the spinners is $O(10 \mu\text{m})$ —in this size regime, the particles form chain-like aggregates.

3.4. Theoretical model

The formation of patterns of disk-shaped spinners can be reproduced by a simple model (Grzybowski et al., 2002a) which treats the spinners as neutrally buoyant and assumes that their motions relative to the fluid are caused by (i) magnetic and pairwise hydrodynamic forces acting in the system, and (ii) the flows created by other spinning particles. Each particle moves relative to the fluid at a velocity U_i proportional to the net force acting on it: $U_i = \zeta^{-1}(F_i^m + \sum_{j \neq i} F_{ij}^h)$, where ζ is a drag coefficient, and in the flow created by the other disks composing an aggregate. Because a single disk j creates a velocity field well approximated by $u_j(x) = a_j^3 \omega \times x/x^3$ (where x is the position vector measured from the spinner's center), the velocity V_i at which any other disk i translates is given by the sum of velocity fields produced by the remaining disks at the location of i : $V_i = \sum_{j \neq i} u_j(r_i - r_j)$. Adding the component velocities U_i and V_i , the equations of motion describing the dynamics of an aggregate composed of N spinning disks can be written as

$$\dot{r}_i = V_i + U_i = \sum_{j \neq i} u_j(r_i - r_j) + \zeta^{-1} \left(F_i^m + \sum_{j \neq i} F_{ij}^h \right), \quad i = 1, \dots, N. \quad (1)$$

3.5. Design considerations

The basic system is based on two competitive interactions, one of which depends on the amount of energy delivered to the system; the system dissipates energy of the rotating magnetic field into the fluid, and changes its internal state (spacing between the disks) in response to the changes in the external flux of energy. It cannot be, however, considered a complex system since simple equations of motion simulate its behavior with excellent accuracy. In order to progress to more complex behaviors, one can either modify the interactions within the plane of the interface and/or try to extend the system into the third dimension. The former can be achieved either by using spinners of different sizes and of shapes less regular than disks or by modifying the profile of the magnetic field. The latter is most easily implemented by placing the rotating particles onto multiple, proximal liquid/liquid interfaces.

4. Complex behaviors in two dimensions

4.1. Symmetry Breaking and Sensitivity to Initial Conditions

When one of the disks in an aggregate is significantly larger than others, some stable assemblies generated in this system are asymmetric, and their morphologies depend on the history of an aggregate—that is, they exhibit hysteresis (Grzybowski and Whitesides, 2004). Fig. 2a shows stable structures formed by one 2.07-mm disk and $N = 4$ –11 smaller disks (1.27 mm in diameter). For $N = 1$ –4, the small disks organize into an “arc” precessing around the large disk. These structures form regardless of whether N disks simultaneously assemble into the final arrangement, or whether one disk is added to a stable $N-1$ configuration.

For $N = 5$ –10, the assemblies exhibit hysteresis. The left column in Fig. 2a shows structures formed from initially randomly distributed disks (“de novo”), and the right column—those obtained when the N th small disk was added to an already organized, stable $N-1$ aggregate. All de novo structures have at least one symmetry plane, and the circular aggregates with $N > 7$ have D_{Nh} symmetries. In contrast, the aggregates obtained by stepwise addition of disks have at most one symmetry plane, and those with $N = 6, 8, 10$ have no symmetry elements—they are asymmetric. The assemblies for $N > 10$ give symmetric, closed-shell structures that do not show hysteresis.

Although numerical simulations based on Eq. (1) reproduce the symmetric de novo assemblies, they do not consistently evolve the disks into asymmetric structures. Specifically, the outcome of these simulations depends strongly on the initial distribution of the disks: for some distributions, symmetric structures emerge, while others lead to asymmetric patterns. We hypothesize that the low-symmetry aggregates arise as a consequence of the interaction between

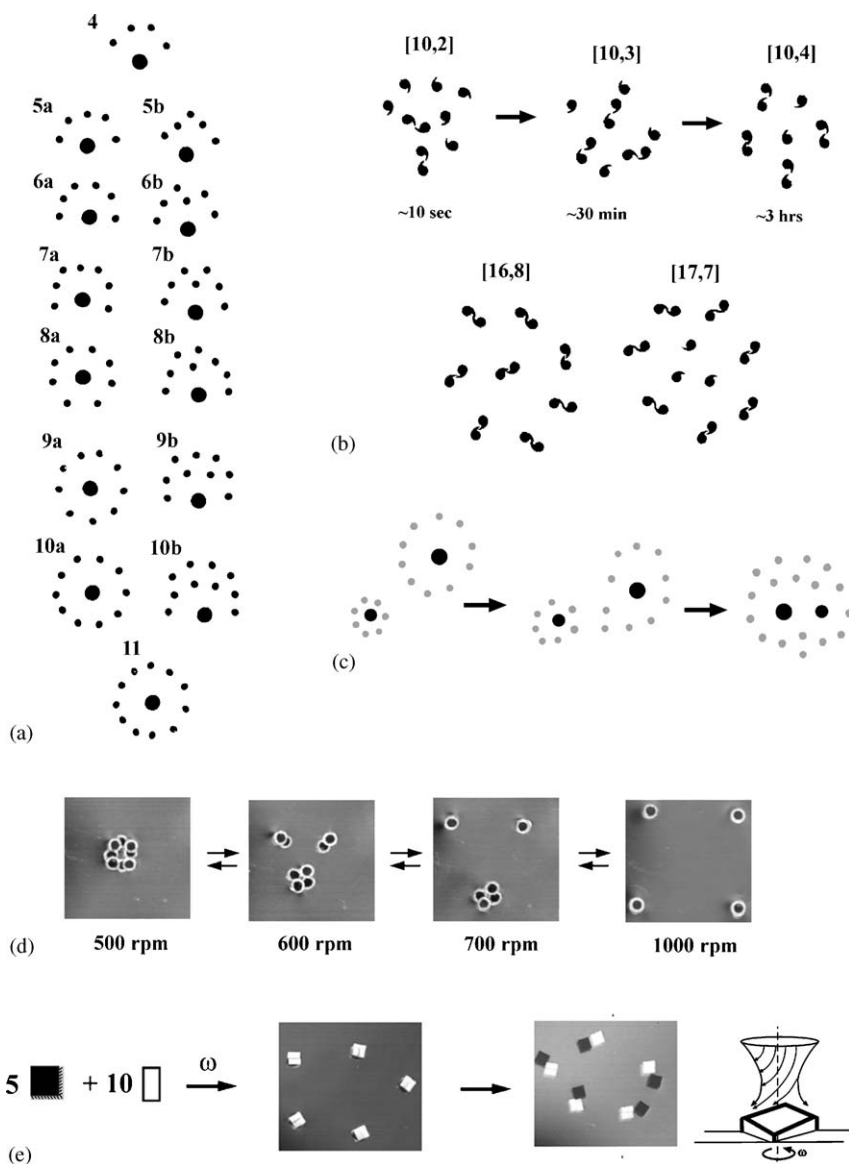


Fig. 2. Complex behaviors in two- and three-dimensional systems of magnetic spinners. (a) shows stable aggregates formed by one large disk (OD 2.07 mm), and $N = 4$ to $N = 11$ smaller disks (OD 1.27 mm); some of the assemblies that form have no elements of symmetry. (b) Pictures in the upper row illustrate the progress of dimerization “reaction” of 10 R plates. The final structures of dimerization reactions of 16 and 17 R plates are shown in the lower row. (c) shows the fusion of two macroscopic “artificial atoms” into an “artificial molecule”. The smaller “atom” is composed of one disk 2.08 mm in diameter, and seven disks 1.27 mm in diameter; 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 created by field concentrators above the plane of the interface, and are “reacted” by moving the concentrators towards each other. (d) illustrates the effect of the angular velocity ω on the morphology of the 3D dynamic patterns. At low ω (~ 300 – 500 rpm), the patterns are “staggered” structures. As the rotational speed increases, the interactions between the disks on different interfaces become attractive: the original patterns disappear, and pairs of disks (one from each interface) form. At $\omega \sim 1000$ rpm, all disks are oriented in pairs connected by columnar vortices (“eclipsed” structure). (e) illustrates the process of pattern replication using vortex–vortex interactions. In these experiments, magnetically doped squares ($2 \text{ mm} \times 2 \text{ mm} \times 1 \text{ mm}$) were spinning on the PFD/EG- H_2O interface at $\omega \sim 700$ rpm, and were used as templates to organize nonmagnetic PDMS rectangles ($2 \text{ mm} \times 1 \text{ mm} \times 1 \text{ mm}$) on the EG- H_2O /air interface into a pattern of squares. The EG layer was 2.5 mm thick. Replication was most efficient when the squares had two of their faces made hydrophobic, so that they were slightly tilted with respect to the PFD/EG interface (schematic graph on the right). The replicated squares remained stable, even when the magnetic field was switched off.

the incoming disk and the global vorticity patch associated with the precession of the existing structure; this interaction is multibody, and models accounting only for pairwise repulsions are inadequate to describe it. We note that (i) the asymmetric aggregates we discussed are one of the sim-

plest experimental systems in which symmetry breaking is observed, and (ii) that complex behaviors in this system result from relatively minor modification of its components (as compared to a fully deterministic system of identical disks).

4.2. Chiral selection

Subtle changes to the shapes of the rotating particles can dramatically change the nature of hydrodynamic forces between them (Grzybowski and Whitesides, 2002a). When comma-shaped plates are placed onto an interface in two non-superimposable/chiral orientations (by analogy to chemical notation, designated as “R” and “S”), they interact stereoselectively. The S commas repel one another and do not aggregate. In contrast, the R commas attract other R commas and form dimers. In aggregates composed of both R and S commas, the R commas dimerize (Fig. 2b), while S commas remain separated monomers.

The attractive interaction between the R commas is multi-body. Each dimerizing pair requires at least one “chaperon” R plate that disturbs the flow in the vicinity of the reacting plates thus allowing them to assume specific mutual orientations required for the dimerization to occur.

4.3. Multistability

Dynamic self-assembly in systems with centrosymmetric magnetic potential always leads to the formation of one aggregate near the axis of rotation of the magnet. In contrast, the success of the synthetic approach to CS we pursue depends on the ability to prepare several coexisting subsystems within the overall system. Such subsystems could be then “reacted” (i.e., interconverted, fused or fragmented) with one another in a fashion similar to that in which chemists react molecules.

We prepared coexisting aggregates of magnetic spinners by modifying the profile of the magnetic field in the plane of the interface (Grzybowski and Whitesides, 2001). Specifically, we placed field concentrators (thin, ferromagnetic needles) above the plane of the interface. These needles deflected the field lines of a rotating bar magnet towards the tip of the concentrator thus changing the magnetic forces acting on the disks in the plane of the interface and creating a local minimum of energy below each concentrator. Disks organized in these minima into stable aggregates that could be moved across the interface by moving the concentrators (Fig. 2c). Aggregates in which one disk was significantly larger than others formed core and shell structures that can be regarded as macroscopic models of the so-called “classical artificial atoms” (Lozovik and Mandelshtam, 1990; Bedanov and Peeters, 1994; Grzybowski et al., 2001a)—that is, as models of microscopic systems composed of finite numbers of interacting classical particles confined by an external field and repelling one another. By moving the concentrators, these “atoms” could be evolved 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”.

5. Complex behaviors in three dimensions

5.1. Three-dimensional patterns and phase transitions

Our experimental system can be extended into the third dimension by placing the rotating particles on two or more parallel, proximal interfaces created by layering immiscible fluids of different densities. Spinning particles create so-called Taylor vortices (Koschmider, 1993) in the fluid above and below the plane of the interface on which they float. These vortex motions give rise to hydrodynamic, “vertical” forces between disks spinning on different interfaces. Interestingly, these forces are repulsive for low values of rotational speeds, and change to attractive when ω is increased. The explanation of this behavior is rather lengthy, and can be found elsewhere (Grzybowski and Whitesides, 2002). For the purpose of the present Review, it is important to note that such qualitative change in the nature of the hydrodynamic forces acting between the layers leads to unexpected phase transitions in the system. Fig. 2d illustrates the changes in the morphology of an [4,4] aggregate composed of eight 1.57 mm disks rotating at two proximal interfaces. For low values of $\omega < \sim 500$ rpm, disks on each interface are arranged into ~ 4 mm \times 4 mm squares that are staggered with respect to each other. When ω is increased to 600 rpm, this structure “melts”, and smaller aggregates are formed (in the picture shown in Fig. 2d—two pairs of disks and a cluster of two pairs). As the angular velocity of disks is increased further, the substructures composed of more than two disks dissociate. Finally, at $\omega \sim 1000$ rpm all disks are arranged in pairs and their axes of rotation are almost aligned. The liquid between two disks constituting a pair forms a columnar vortex that “glues” the disks together. The aggregate forming at 1000 rpm is a square with four aligned pairs positioned in its vertices (“eclipsed” structure).

5.2. Pattern replication

As in the case of forces within one interface, the forces between the interfaces can be modified by changing the shapes of the interacting particles (Grzybowski and Whitesides, 2002b). In particular, for certain shapes it is possible to engineer these “vertical” forces such that the particles rotating at one interface direct the assembly of the particles at the other. A striking example of such a design is a system (Grzybowski and Whitesides, 2002b) in which a pattern of magnetized squares at one interface directs the assembly of nonmagnetic rectangles at another interface into its own replica (Fig. 2e).

The replication process is the consequence of the interplay between (i) the attraction of the non-magnetic substrates towards the vortex produced by the templates, and (ii) the hydrodynamic repulsion between the substrates rotating under the influence of templates. Initially, when a template has no substrates associated with it, the only

interaction experienced by the substrates is the attraction towards the vortex produced by the template. When a template engages one substrate, the substrate starts spinning under the influence of the vortex. This spinning results in a repulsive hydrodynamic force acting on other substrates floating on the upper interface. The repulsion is, however, smaller than the attraction by a template, so that one more substrate can be engaged. When this happens, the dimer spinning in the vortex produces hydrodynamic repulsive force that offsets the attraction by the template vortex. Consequently, no more substrates can be engaged, and the replication is complete.

6. Summary

Each of the systems we described has some features that make them relevant to the subject of complexity: they are all based on non-linear interactions, they are very hard—if not impossible—to describe by exact mathematical models, and some of them exhibit unexpected/emergent behaviors (e.g., chiral discrimination or pattern replication). Yet, we do intuitively feel that these systems are but building blocks *en route* to truly complex assemblies, which could evolve, adapt and perform purposeful functions.

Such functional systems can be designed even with a limited repertoire of hydrodynamic and magnetic forces, and some—still relatively simple—examples will be described in the next section. Moreover, given a large number of forces/phenomena suitable for the synthetic approach to CS we pursue (cf. Table 1), we are convinced that the number of model complex systems and ensuing functional devices will steadily grow. Once classes of systems based on different types of interactions are prepared, it will be necessary to formulate rules allowing putting these classes together. For example, can a magnetohydrodynamic and an electrostatic sub-systems be combined into a higher-order CS? What are the synthetic rules that would allow such combination? The answers to such questions will allow our approach to mature to the point where it is loosely analogous to the practice of organic chemistry: instead of complex molecules, however, we will be able to synthesize systems-of-systems.

6.1. Coda: towards the applications

From a technological point of view, CS are—owing to their ability to respond to external stimuli—promising candidates for new types of reconfigurable sensory and mechanical devices. To fulfill this promise, fundamental research on physical CS should be accompanied by an effort to develop at least some of these systems into applications. In the remaining part of our Contribution, we will describe how systems based on magnetic and hydrodynamic interactions can be engineered to perform useful mechanical functions. We present these examples somewhat in lieu of a traditional “Outlook” section, for the future of the dynamic CS is largely dependent on whether they will ultimately lead

to useful applications. If they do, dynamic CS and the synthetic strategy of making them will enter the mainstream of modern science; if not, they will remain an interesting “curiosity” at its periphery. We believe that simple devices we describe are the first step in the first direction.

6.1.1. Hydrodynamic membranes

Fig. 3a shows a self-assembled aggregate of spinning disks that acts as a “hydrodynamic membrane” sorting small (tens of micrometers) particles according to their size. In the picture shown here, polystyrene spheres of two sizes (20 and 40 μm) are floating at the interface between soap water and air. When the disks are placed at the interface and their rotational speed is increased to ~ 700 rpm, all particles are expelled from the high-pressure region inside the aggregate. When ω is reduced to ~ 600 rpm, the momentum imparted on small particles (and to lesser extent on the large ones) is enough to carry some of them from the outside of the aggregate inwards, through the region of high pressure between the disks. More small than large particles penetrate the outer shell of the aggregate. Some of these particles are further filtered into the inner “rhomboidal” part of the structure when they remain trapped within a closed loop of circulation; more than 95% of them are the 20 μm spheres. Hydrodynamic membranes like the one described above can be tuned to filter particles of different sizes by changing the rotational speeds, sizes and numbers of disks (numbers of shells).

6.1.2. Self-assembled fluidic machines

Vortex–vortex interactions are the basis of self-assembly of systems of gears performing simple mechanical functions (Ng et al., 2003; Grzybowski et al., 2004). Power from the external, rotating magnetic field is harnessed by two-component rotors composed of a magnetic core and a non-magnetic gear-shaped ring around it. When the magnet rotates, the cores center inside the gears and set them on rotary motion. The positions of the rotors at the interface are controlled by localized magnetic fields produced by an array of electromagnets immersed in the liquid. Because the fluid motion associated with the rotation of the rotors gives rise to hydrodynamic repulsions between them, no two rotors can aggregate above the same electromagnet. Thus, for a given configuration of active electromagnets, the rotors always self-assemble into a unique structure, and the configuration of the machine (and its function) is uniquely determined by the arrangement of active electromagnets.

Fig. 3b shows a rotary carousel system that manipulated small containers floating at the surface of the liquid. This device comprised seven rotors organizing above an array of 19 electromagnets (Fig. 3b(i)). The containers to be manipulated were nonmagnetic PDMS rings dyed blue (for ease of identification) filled with mineral oil. Initially, the rotors organized into a symmetric hexagonal structure, and the reactors floated outside of this structure. When two

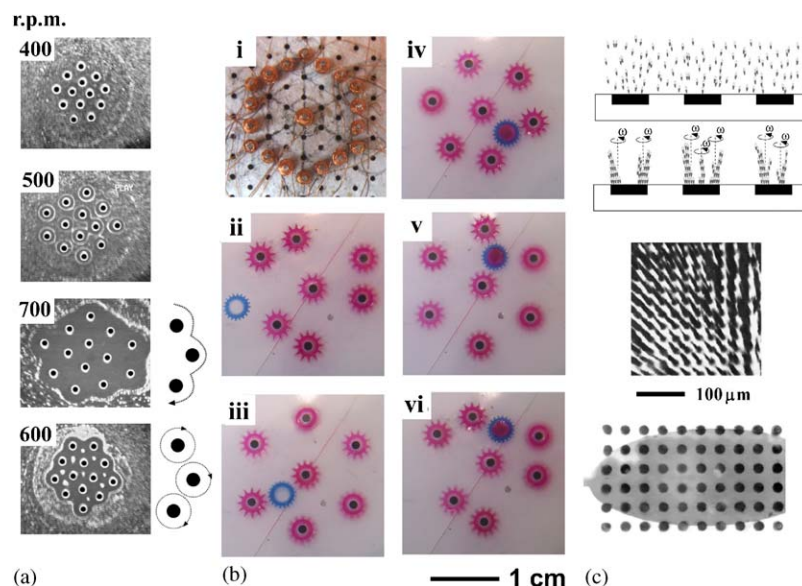


Fig. 3. Examples of fluidic applications based on assemblies of rotating particles. (a) A hydrodynamic membrane composed of 13 1 mm magnetic disks and sorting polymeric microspheres floating at the interface according to their size. (b) (i) shows 19 electromagnets (200 coils each, 0.5 A per electromagnet) used in the carousel system. Seven gears organize above these electromagnets to manipulate nonmagnetic containers floating at the interface. The carousel first incorporates an empty container (ii), turns it around (iii) until the filling point (iv), completes the revolution (v), expels the filled container (vi), and finally returns to its initial state. The motions of the carousel are caused by synchronous activation of the electromagnets: When the carousel opens or closes, three electromagnets are simultaneously turned on; when the carousel rotates, six electromagnets are activated at a time. (c) Microfluidic mixer. The upper two pictures illustrate aggregation of magnetic particles from initially uniform dispersion in the fluid into needle-like aggregates above the concentrators. Each needle rotates with angular velocity ω equal to that of the external rotating magnet. Several needles form over large concentrators; smaller concentrators ($< \sim 50 \mu\text{m}$) have exactly one, conical needle above each concentrator (middle picture). An optical micrograph of an array of micromixers in an oval-shaped chamber achieves an almost complete mixing of laminarly in-flowing fluids.

neighboring, outer-layer rotors were moved slightly apart from each other (Fig. 3b(ii)), a single reactor could be transferred into the carousel. The carousel then turned around by synchronous activation of the electromagnets, and the container moved with the rotating carousel (Fig. 3b(iii)). After an approximately 180° rotation, the reactor passed above a thin needle that was connected to a syringe pump, and that delivered mineral oil dyed with rhodamine (Fig. 3b(iv)). After the application of the desired amount of the colored solution (usually $10 \mu\text{l}$), the carousel turned another $\sim 120^\circ$ (Fig. 3b-v), and then opened to liberate the reactor (Fig. 3b-vi). The device then returned to its original state, and was ready to manipulate another container.

6.1.3. Microfluidic mixers

In this device, ferromagnetic spinners organized inside a microfluidic channel into an array of efficient micromixers (Campbell and Grzybowski, 2004). The device was fabricated from poly (dimethylsiloxane) and had small magnetic flux concentrators fabricated at its bottom by micro transfer molding technique.

When a permanent bar magnet rotated below a device, and when a solution containing small ferromagnetic particles (iron filings, $\sim 5 \mu\text{m}$ in diameter) was flown through the channel, polarized the particles and they aggregated above

the concentrators into needle-like aggregates (Fig. 3c). Within each needle, the particles were held together by magnetic dipole–dipole interactions. As the needles organized, they created vortices in the surrounding fluid that interacted repulsively with the vortices generated by the remaining magnetic particles in solution. At a given instant, these repulsions pushed the free particles onto smaller needles so that, in the end, all needles were approximately of the same size. The needles pointed in the direction of the external magnetic field (approximately vertical), and rotated around their bases with angular velocity ω equal to that of the external rotating magnet. At high values of ω , the arrays of rotating spikes achieved complete mixing of fluids laminarly flown through the channel

The micromixer described here is an example of an application in which self-assembly significantly simplifies microfabrication and leads to a device with excellent working characteristics. This system illustrates well one of the major advantages of the synthetic approach to CS: Even though the physics underlying the system is certainly complex, it is remarkably easy to engineer via a “synthesis” of several phenomena described earlier in this work.

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