

FEATURE ARTICLE

Principles and Implementations of Dissipative (Dynamic) Self-Assembly

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Dynamic self-assembly (DySA) processes occurring outside of thermodynamic equilibrium underlie many forms of adaptive and intelligent behaviors in natural systems. Relatively little, however, is known about the principles that govern DySA and the ways in which it can be extended to artificial ensembles. This article discusses recent advances in both the theory and the practice of nonequilibrium self-assembly. It is argued that a union of ideas from thermodynamics and dynamic systems' theory can provide a general description of DySA. In parallel, heuristic design rules can be used to construct DySA systems of increasing complexities based on a variety of suitable interactions/potentials on length scales from nanoscopic to macroscopic. Applications of these rules to magnetohydrodynamic DySA are also discussed.

1. Introduction

Self-assembly (Figure 1), that is, the process by which isolated components organize autonomously and spontaneously into ordered and/or functional structures,¹ is nature's preferred way of building its animate creations on various length scales. DNA strands self-assemble into a double helix that stores genetic information; various proteins organize into multiprotein complexes which enable transcription,^{2,3} translation,^{4,5} RNA splicing,⁶ signaling,⁷ exocytosis,⁸ RNA interference,^{9,10} and numerous other cellular processes; cellular membranes self-assemble from phospholipids, cholesterol, glycolipids, and protein building blocks to delineate the cell's boundary through which it interacts with its environment; cells spontaneously organize into tissues,¹¹ bacteria into colonies,^{12,13} and higher organisms into swarms,¹⁴ schools¹⁵ or flocks.¹⁶

Science and technology have long recognized the promise of the "bioinspired" self-assembly (SA) approach for building large structures from small objects. In molecular sciences, SA lies at the heart of supramolecular chemistry,^{17,18} where the "instructions" of how to assemble larger entities are "coded" in the structural motifs of individual molecules. In nanotechnology, SA underlies various types of molecular structures (e.g., Langmuir–Blodgett films,¹⁹ self-assembled monolayers,^{20–22} amphiphilic fibers^{23,24}) as well as higher order architectures built from nanoparticles,^{25–28} nanotubes,²⁹ or nanorods,³⁰ and has also been extended to mesoscale assemblies of colloidal/microscopic particles.^{31,32} Some of these approaches are already finding industrial applications. For example, Alien Technologies has developed fluidic self-assembly techniques to fabricate electronic components, such as radio frequency identification tags, by using shape recognition and fluid transport on the microscale;^{33,34} Nanogen employs electric field-mediated self-assembly to bring

together DNA nanocomponents for electronic and diagnostic devices.³⁵ In all of the above examples, SA capitalizes on the fact that with the current state of chemistry/material science it is easier to "program" individual particles and let nature do the difficult rest rather than to position very small components (e.g., by optical tweezers³⁶ or atomic traps³⁷) or modify tiny structures (e.g., by STM³⁸).

Despite several impressive demonstrations, such as SA of 2D and 3D structures via capillary forces,^{39,40} DNA templating,^{41,42} microfluidic SA,⁴³ SA of electronic circuits,^{44,45} fluidic machines,⁴⁶ microfluidic micromixers,⁴⁷ microspheres with complex internal structures,⁴⁸ 2D electrostatic crystals,^{49,50} and supramolecular templates for the synthesis of novel chemical compounds,⁵¹ we are still very far from using SA as flexibly and creatively as nature does. In a vast majority of man-engineered SA systems, the structures that emerge are ordered but static; once made, they cannot be further adjusted/reconfigured, and cannot perform different functions depending on the changes in external parameters. They are "crystals," not "cells." In real cells, tissues, and organisms, SA builds dynamic aggregates that change and function only if energy is delivered to them — either chemically or by external fields. Generalizing, most biological forms of adaptive or intelligent behavior and self-replication are based on dynamic self-assembly (DySA), in which the mode of organization depends on the amount of energy delivered to the system. If we were to mimic such behaviors in artificial systems, we must first understand the principles that govern DySA. This contribution is intended to initiate the search for such an understanding. As we will see, relatively little is known about the subject — both in theory and in experiments. Consequently, our discussion will sometimes use qualitative and heuristic arguments, which, while short of being fundamental, prove useful in designing DySA systems.

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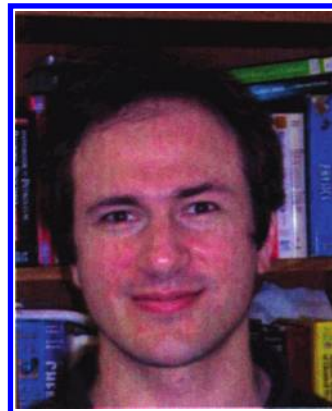
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2. Static and Dynamic Self-Assembly – Definitions

Before addressing DySA in detail, it is first necessary to define exactly what is meant by self-assembly in general. Within the burgeoning field of “self-assembly” – from supramolecular chemistry^{52–54} to the rings of Saturn⁵⁵ – one frequently finds informal definitions that are consistently manipulated to make room for the latest interesting phenomena. Here, we limit SA to the spontaneous formation of organized structures from many discrete components that interact with one another directly (e.g., electrostatic interactions between charged objects⁴⁹) and/or indirectly through their environment (e.g., chemotactic interactions between bacteria, which create and respond to chemical gradients in a surrounding medium^{12,13}). In addition, the assembling components may also be subject to various global (confining) potentials such as externally imposed electromagnetic fields or chemical gradients. By constraining our definition of SA to organized structures, in which preexisting components interact reversibly and in a controllable way, we distinguish SA proper from a broader class of “aggregation” processes, such as precipitation reactions,⁵⁶ Ostwald ripening/coagulation,⁵⁷ or ballistic deposition on surfaces.⁵⁸ Furthermore, since we stipulate that the components of SA be discrete objects whose assembly cannot be described by a continuum approach (generally, they can be described as a dispersed/discontinuous phase distributed in some continuous medium), we strictly exclude pattern formation in continuous media (e.g., chemical waves,^{59–61} Turing patterns,^{62,63} Benard convection^{64,65}).

Within the above definition, there exist two major classes of SA systems: static self-assembly (SSA; Figure 1a) and dynamic self-assembly (DySA; Figure 1b). The distinction between SSA and DySA refers to the thermodynamic description of the resulting assemblies (Figure 1c), the former being equilibrium structures (in either global or local equilibrium) and the latter, stable nonequilibrium structures maintained in a steady state by a constant supply of energy, which is subsequently dissipated via the entropy producing (i.e., irreversible) processes associated with the interactions of the system’s components. It is stressed that these definitions refer only to the final self-assembled structure and not to the SA processes by which such structures were achieved; in fact, SSA often requires nonequilibrium processing/agitation to generate stable structures characterized by zero entropy production.^{49,66}

To form dynamic SA structures, one must drive the system away from equilibrium by supplying energy, which sets up and/or modifies the interactions of the building blocks with each other and with the environment. Such DySA structures represent a subset of a broader class of “dissipative” structures,⁶⁷ in which the production of entropy directs the emergence of order. Examples of DySA, extensively described in Table 2, include electrorheological fluids,⁶⁸ magnetorheological fluids,⁶⁹ and magnetohydrodynamic self-assembly.⁷⁰ These dynamic structures rely on a constant energy supply for survival and collapse (“die”) when the flow of energy ceases.

3. Thermodynamics of DySA – A Theory in the Making

In terms of fundamental thermodynamic characteristics, DySA structures belong to a broad class of nonequilibrium (NE) steady-state systems. Although these systems have been studied intensively for several decades,^{67,71–74} they are still poorly understood, mostly because of the lack of general variational principles governing their behaviors. Importantly, since the fundamental law of entropy maximization is not valid in the nonequilibrium regime, DySA systems can “reside” in low entropy states and are able to organize themselves into complex

spatial or coherent spatio-temporal structures,^{67,71} which can be maintained only by dissipating energy into the environment and thus increasing its entropy.

For NE systems close to equilibrium, Prigogine⁶⁷ proposed his famous variational principle, called the Minimal Entropy Production (MEP) rule. If the change, dS , of the system’s total entropy is written as a sum of entropy produced in this system by irreversible processes, dS_P , and the entropy flow due to exchange of energy or work between the system and its environment, dS_E , then the MEP rule stipulates that the rate of entropy production, $P = dS_P/dt$, is minimal at steady state (and, of course, $dS = 0$ therein). While this law has proven remarkably useful in many cases,^{67,71} it must be remembered that it applies only to “linear nonequilibrium thermodynamics,”⁷¹ where the Onsager’s reciprocal relations⁷¹ hold, and the assumption about local thermodynamic equilibrium is valid. Unfortunately, in the linear regime, the system is uniform and dissipative structures are not observed.⁶⁷ They appear only far from equilibrium, when the “linear” steady-state becomes unstable, and the system “switches” to an ordered configuration via a bifurcation mechanism^{67,71} induced by changes in external forces/parameters (e.g., the frequency of rotating magnetic field in the case of self-assembling spinners; cf. section 6).

NE systems driven beyond the linear regime have recently been studied on the microscopic level, using both numerical^{75–79} and analytical^{180–83} tools of statistical mechanics. It appears that a very promising way to describe these systems is to explore the properties of their phase space.^{72,74} Within this approach, the second law of thermodynamics governing the system’s evolution can be related to the geometry and topology of the phase space. Specifically, when a NE system described by deterministic equations of motion evolves (Figure 2a), its phase space probability distribution function, $f(\Gamma(t), t)$, collapses (“shrinks”). For a system of N particles, $f(\Gamma(t), t)$ is a function of the space vector, $\Gamma(t) = (\mathbf{q}_1(t), \dots, \mathbf{q}_N(t); \mathbf{p}_1(t), \dots, \mathbf{p}_N(t))$, where $\mathbf{q}_i(t)$ and $\mathbf{p}_i(t)$ stand, respectively, for the position and momentum of the i th particle. Eventually, the system reaches its nonequilibrium steady state with phase space characterized by a complicated set of fractal structures called a strange attractor^{72,84} (Figure 2b). Phase space compression is related to the loss of the system’s dimensionality,^{72,74,77} and is facilitated by a continuous flow of entropy, which is transferred from the system to its surroundings. In other words, as the system organizes itself, the phase space available to its components becomes smaller, and the larger the change in the degree of system’s ordering (per unit time), the more entropy is produced and transferred to the environment.

An illustrative example of phase space compression is provided by a model DySA system (cf. section 6) of magnetically driven “spinners” interacting by vortex–vortex interactions (Figure 2c). The random initial configuration of N such spinners occupies a $4N$ -dimensional phase space. As the spinners organize into a regular, rotating open lattice, the dimensionality of the phase space is significantly reduced to an effective dimension close to one (corresponding to the angular position of the lattice). Importantly, however, this dimension is not equal to one since individual disks are not frozen in their positions in the lattice and can randomly exchange with their neighbors; in terms of the phase space, we say that the system is at a strange attractor.

Of course, it would be highly desirable to recast these qualitative arguments into a functional form. In this context, two possible variational principles governing the time evolution of a system far from equilibrium have been considered. The

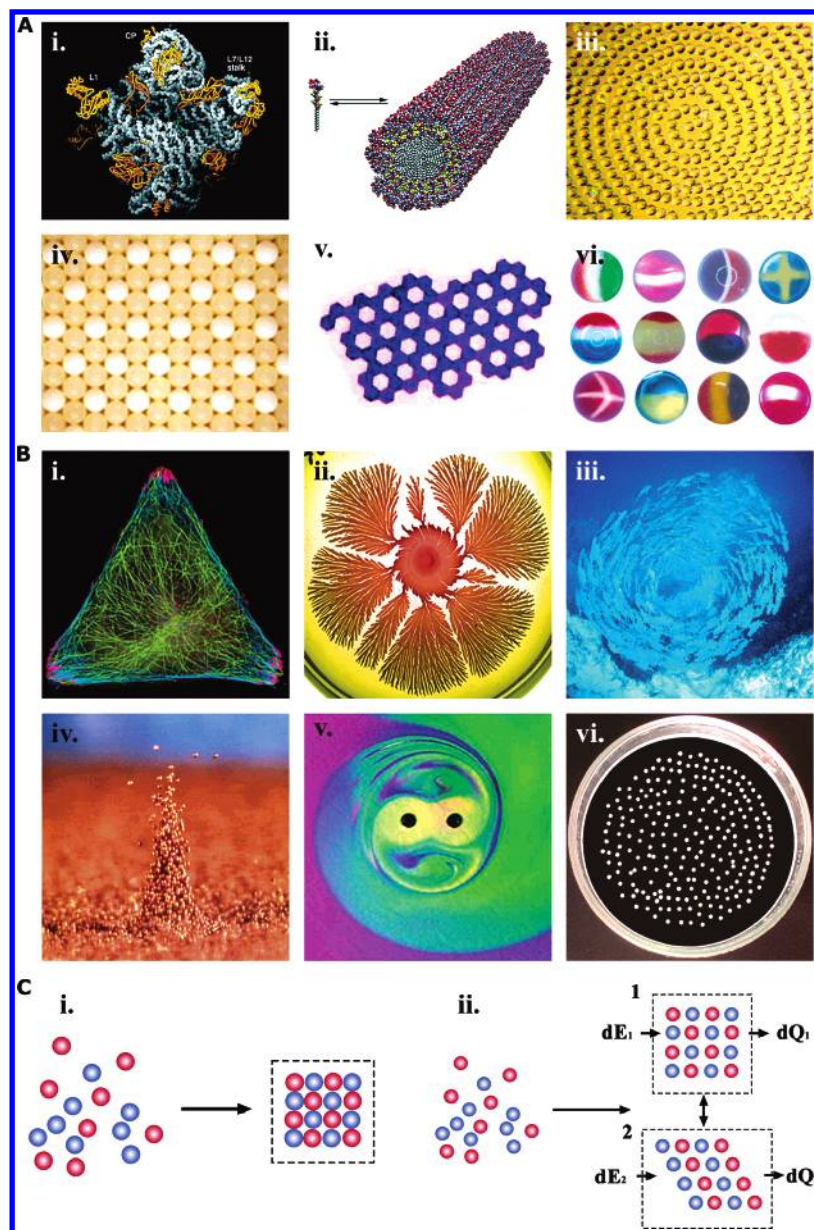


Figure 1. Examples of self-assembly (A) static self-assembly and (B) dynamic self-assembly. (A)(i) Crystal structure of a ribosome. (ii) Self-assembled peptide-amphiphile nanofibers. (iii) Electrostatic self-assembly (ESA) of polymeric microspheres on a charge-exchanging substrate modified by wet stamping. (iv) ESA of macroscopic 2D crystals whose formation is mediated by charges developed by contact electrification. (v) Capillary SA of polymeric plates at an interface between two liquids. (vi) Self-assembled polymeric microspheres of complex internal structures. [Reprinted with permission from (i) ref 132, (ii) ref 23, (iii) ref 133, (iv) ref 49, (v) ref 40, (vi) ref 48]. (B) Examples of dynamic self-assembly in living (i–iii) and artificial systems (iv–vii). (i) Fluorescently labeled microtubules in a cell confined to a 40 μm triangle on a SAM-patterned surface of gold (staining scheme: green = microtubules, red = focal adhesions, blue = actin filaments). (ii) Bacterial colony growth. (iii) School of fish. (iv) Oscillation of vibrating metal beads. (v) Vortex–vortex interaction via magnetohydrodynamic dynamic self-assembly. (vi) Surfactant-mediated dynamic self-assembly of gel particles floating at a liquid/air interface. Leaking of a surface-active compound the particles carry onto the interface gives rise to dynamic (repulsive) capillary forces acting between the objects. [Credits: (i) K. Kandere-Grzybowski, Northwestern University (ii) E. Ben-Jacob, Tel Aviv University. (iii) Reprinted with permission from ref 1. (iv) P. Umbanhowar, Northwestern University. (v) Reprinted with permission from ref 93. (vi) K. J. M. Bishop & B. A. Grzybowski, unpublished results.] (C) Schematic representation of (i) static and (ii) dynamic self-assembly. (i) In static self-assembly, components form an ordered aggregate whose structure does not change. (ii) Dynamic self-assembly evolves a disordered collection of components into an ordered structure through input of energy from an external source and dissipates this energy (e.g., as heat). The system generates entropy, which is being continuously transferred to the environment. The system can realize different configurations dependent on the rate of energy input, and when no energy is driving the system, it “falls apart.”

first one is based on recent molecular-dynamics simulations of particles in a shearing flow,^{73,76} and proposes that a steady-state removed from equilibrium by some external field is determined by the minimum of the average phase space compression factor, $\langle \Lambda(t) \rangle = -\langle d \ln(f(t))/dt \rangle$. This minimum compression rule (MCR) should hold even for systems far from equilibrium, where the local thermodynamic equilibrium breaks down. Interestingly, in the linear nonequilibrium regime the quantity $-k_B \langle \Lambda(t) \rangle / 2$ represents exactly the entropy production

rate, P , due to the external field, and the MCR becomes equivalent to Prigogine’s MEP principle.

The second approach is based on Lyapunov exponents^{72,74,85} and seems better suited for the description of DySA. Briefly, the Lyapunov exponent, λ , is a mathematical concept that characterizes the rate of separation of infinitesimally close trajectories in the phase space. In the simplest case of a one-dimensional dynamical system, there exists only one Lyapunov exponent, λ , which measures how rapidly the distance between

TABLE 1: Examples of Dynamic Potentials

Confining Potential	Scaling Characteristics, Parameters, Limitations	Applications and References
Optical Traps ³⁶ 1D, 2D, and 3D	<ul style="list-style-type: none"> * Gradients of light intensity direct organization of dielectric particles whose sizes can range from ~ 5 nm to ~ 500 μm. * In the Rayleigh limit, $ka \ll 1$ where k is the wave number and a is the radius of the particle, $F \sim (a/2)\nabla E^2$. * Potential can be approximated as quadratic. * Trapping works only if the index of refraction of trapped particle(s) is higher than that of a surrounding medium. * Metallic particles can be trapped due to their high polarizability. * For optical trapping, the energy of interaction must be large compared to thermal energy, $k_B T$, and kinetic energy of particles must be dissipated, e.g., by “optical molasses” for atoms or by fluid viscosity for micron-sized particles. 	<p>Various techniques using optical forces: Single beam optical tweezers;^{140,141} Scanned optical tweezers;^{142,143} Holographic optical tweezers;^{144,145} Standing waves by beam interference (e.g., “optical matter”);^{146–149}</p> <p>Applications: Trapping and crystallization of atoms;^{150–153} Formation of 2D^{144,145,147} and 3D¹⁵⁴ crystals of colloidal particles; Sorting of particles by size and/or refractive index using dynamic 3D optical lattices;^{155,156} Manipulation of cells,^{157,158} viruses¹⁵⁸ and biological molecules;^{159–161} Studies of molecular motors;^{162–164} Microsurgery;^{165,166} Actuation of microdevices.¹⁶⁷</p>
Rotating Magnetic Fields 2D	<ul style="list-style-type: none"> * A rotating bar magnet of length L exerts a force on a magnetic particle that scales as $F_m \sim a^3 r$ in the limit of $r \ll L$, where r is the distance from the axis of rotation and a is the radius of the particle. The force is directed toward the axis of rotation. 	<p>DySA of disks at liquid–air and liquid–liquid interfaces;^{70,93–95,111–113} Self-assembling micromachines^{46,114} and microfluidic devices.⁴⁷</p>
Confining Magnetic Fields 1D and 2D	<ul style="list-style-type: none"> * The force generated by two Helmholtz coils situated in the y-z plane perpendicular to the x-axis at $x = 0$ and $x = R$ scales with the magnetic field, B_x, as $F \sim m(\partial B_x/\partial x)$ and $B = (\mu_0/2) IR^2(1/((R^2 + (x - R)^2)^{3/2}) + 1/((R^2 + x^2)^{3/2}))$, where μ_0 is the permeability constant, I is the current running through the coils in the same direction, and x is the location of the particle. 	<p>Magnetic tweezer for ferromagnetic beads,^{168,169} magnetic atomic trap.¹⁶⁹</p>
Centripetal Forces 2D and 3D	<ul style="list-style-type: none"> * $F_c = mv^2/r$, where v^2/r is the centripetal acceleration * Confines particles of densities less than surrounding fluid 	<p>Aggregation of millimeter-sized hollow beads in ethylene glycol;¹⁷⁰ Simulation of centripetal packing of spheres;¹⁷¹ Diffusion-limited aggregation of crystals in electrodeposition.¹⁷²</p>
Acoustic Waves 2D	<ul style="list-style-type: none"> * For shallow fluids, the wavelength of Faraday waves can be determined by $\lambda = (16\pi^2(\sigma/\rho)f_e^2H)^{1/4}$, where σ is the surface tension, ρ is the density, f_e is the frequency of the driving force, and H is the thickness of the liquid. * Edge effects can cause distortions and lead to deviations from the above formula. 	<p>Patterning of particulate films from vibrating liquids;¹⁷³ Oscillon formation in vibrated granular layers;¹⁷⁴ Simulations of vibration-induced granular self-assembly;¹⁷⁵ Dynamic hole formation in vibrated liquid layers and in layers of glass microspheres.¹⁷⁶</p>
Convective Flows 1D, 2D, and 3D	<ul style="list-style-type: none"> * Rayleigh-Benard convection (i.e., convection rolls) occurs when the thermal instability of buoyancy overcomes viscous forces, when the Rayleigh number, $R_a = \alpha\beta g d^4/k\nu \gg 1$, where α is the coefficient of thermal expansion, β is the thermal gradient over the depth, d, of the chamber, g is acceleration due to gravity, k is the thermal diffusivity, and ν is the kinematic viscosity. * Rolls created by Rayleigh-Benard convection create confining potentials, where particles can become trapped if the downward viscous forces do not exhibit enough force to overcome the buoyancy of the particle 	<p>Laser-induced coalescence of emulsions;¹⁷⁷ Thermal-convection enhanced segregation;¹⁷⁸ Dynamic self-assembly of vesicles in microfluidic flow fields.¹⁷⁹</p>
Electrostatic Confinement 2D and 3D	<ul style="list-style-type: none"> * In 2D arrangements, charged particles in a plane (e.g. floating on the surface of a liquid) and confined radially by an electrostatic field. In a 3D variation, confinement involves a charged disk under the particles to counteract gravity, while a charged ring confines them in the horizontal plane. Thus the particles are restricted to a conical potential well. * A new effect, that is only produced near a charged wall,¹⁸⁰ involves clustering of like-charged particles in the absence of confinement from other directions.¹⁸¹ Both experiments and modeling over the last 20 years continue to clarify this effect,^{182–185} which cannot be explained with the mean-field Poisson–Boltzmann theory¹⁸⁶ * Hydrodynamic interactions¹⁸⁷ and configurational temperature concepts¹⁸² have been invoked in order to explain the effect. 	<ul style="list-style-type: none"> * Charge confinement, combined with repulsion between charged particles can induce their ordering into lattices¹⁸⁸ * 3D ordered arrangements of particles were observed in plasma confinement within a charged ring and above a charged disk to counteract gravity.¹⁸⁹

two neighboring points in the phase space is growing with time. Quantitatively, the distance $|\delta\Gamma(t)|$ between these two points, which are initially separated by the vector $\delta\Gamma_0$, changes with time as $|\delta\Gamma(t)| \sim \exp(\lambda t)|\delta\Gamma_0|$ (cf. Figure 2a). If λ is positive, then any two neighboring trajectories diverge and the system is chaotic and unstable (also, the larger the exponent's value, the more sensitive is the system to initial conditions). If λ is negative, then the system is dissipative and attracts to a fixed point or stable periodic orbit. If $\lambda = 0$, a volume element of the phase space does not change along the trajectory and the density of the phase space is conserved. In the general case of an

n -dimensional phase space, the rate of separation of the trajectories can be different for different orientations of the phase space vector. The system is then characterized by a set of Lyapunov exponents, $\{\lambda_i\}$, where $i = 1, 2, \dots, n$.

There is a close relation between properties of NE dynamical systems and their Lyapunov spectra. Specifically, it can be shown^{72,73,77} that if a system is dissipative, its phase space density collapses during the evolution, and the sum of all Lyapunov exponents is negative (and is equal to zero if the system is conservative). The shrinkage of the phase space leads to the formation of ordered DySA structures and is driven by

TABLE 2: Examples of Dynamic Forces

Interaction	Induced/Addressed by	Particle Size/Type	Applications and References
Induced magnetic Dipole–dipole ¹²⁹	* Induced by external magnetic field. * Interparticle force scales as $F_{ij} \sim \sigma^6 H_0^2 / R_{ij}^4$ where σ is the particle size, H_0 is the strength of the applied magnetic field, R_{ij} is the particle separation.	Colloidal 0.1–100 μm ferromagnetic	SA microfluidic mixers; ⁴⁷ Applications of magnetorheological fluids: automotive clutches, ¹⁹⁰ polishing fluids, ¹⁹¹ smart knee prosthetics, ¹⁹² anti-lock brakes, ¹⁹³ vibration control of washing machines, ¹⁹⁴ 2D and 3D arrays of electromagnetorheological colloids, ^{195,196} active seismic control of buildings. ^{197–202}
Optical Binding	* Intense optical fields induce long-range forces between dielectric particles. * The interparticle potential is approximated by $W = -1/2\alpha^2 E^2 (2\pi/\lambda)^2 \cos(2\pi r/\lambda)/r$ where α is the polarizability of the particle, E is the electric field, λ is the wavelength, and r the interparticle separation.	Colloidal 0.1–100 μm	Formation of ordered 2D crystalline arrays of colloidal particles which are held together by light. ^{147,203}
2D Vortex–vortex	* Hydrodynamic flows induced by objects rotating in a fluid create a repulsive force perpendicular to the axis of rotation. * The force scales as $F \sim \rho\omega^2 a^7/d^3$, where ρ is the fluid density, ω is the angular velocity, a is the characteristic dimension of the object, and d is the interobject distance.	μm –mm sized objects	DySA of magnetized disks at a liquid–air interface; ^{70,94,111–113} Self-assembled gear systems and fluidic machines; ^{46,114} Cell membranes with SA arrays of rotating biomotors; ²⁰⁴ Vortex crystals in magnetized electron columns. ^{205,206}
Flow-induced viscous interaction	If two porous spherical particles are moving along their line of centers with relative velocity u , the viscous force ²⁰⁷ between them is $F_v \sim \mu u R^2/h$, where μ is viscosity of the fluid, and h is the distance between the surfaces of the spheres. Consequently, in the presence of a flow, the particles are effectively driven together to equal their relative velocities.	μm –mm sized objects	Flow-induced structures in sheared colloidal suspensions. ²⁰⁸
3D vortex columns	* Objects rotating above/below one another at two fluid–fluid interfaces experience a repulsive force F_R at low angular velocity ω and an attractive force F_A at high ω . * These forces scale as $F_R \sim \omega^{3/2} \exp(-c h \omega^{1/2})/d^3$ and $F_A \sim \omega/d^2$ where h is the thickness of the fluid phase between the objects, d is the horizontal inter-object distance, and c is a constant.	μm –mm sized objects	DySA of 3D vortex crystals. ^{93,95}
Dynamic Capillary	* Gradients in temperature or the concentration of surface-active agents create nonhomogeneous surface tension profiles on a fluid–fluid interface – Marangoni effect. * Repulsive interparticle forces are created when the particles themselves generate such gradients at an interface on which they are free to move.	μm –mm sized objects	Dynamic self-assembly of camphor-doped polymeric particles at the fluid–air interface; ²⁰⁹ Dynamic behavior of camphor particles at the fluid–air interface: spontaneous movement, ²¹⁰ oscillations and symmetry-breaking, ²¹¹ mode selection and synchronization of two camphor boats. ²¹³
Induced electric dipole–dipole ⁶⁸	DC and AC voltages up to 100 kHz, $F_{ij} \propto \sigma^6 E_0^2 / R_{ij}^4$ where σ is the particle size, E_0 is the applied field, R_{ij} is the particle separation	0.1–100 μm semiconductor particles	Applications of electrorheological fluids: Ordered arrays of colloidal particles; ²¹⁴ Smart inks; ^{215–217} Mechanical polishing; ^{218,219} Tactile displays; ²²⁰ Actuators; ²²¹ Dynamic self-assembly in electrostatically driven granular media: crystals, rotating vortices, and pulsating rings. ^{222,223}
Charge–charge via contact electrification	* The force between two charged particles is $F = k q_a q_b / r^2$, where k is the Coulomb force constant, r is the distance between the particles, and q_a and q_b are the respective charges of particles a and b . * Electrostatic charges can be generated by contact electrification, and the resulting forces scale with surface area. ⁴⁹ * Dissipation of charge is necessary to build dynamic structures and can be achieved by corona discharge in humid conditions, in which the stream of positive and negative ions neutralizes charge built-up. ²²⁴	Submicron to millimeter scale, polymeric or metal	Electrostatic self-assembly of macroscopic crystals using contact electrification; ⁴⁹ Control of contact charging by adjusting humidity; ²²⁴ DySA of rings of charged metal spheres; ⁶⁶ Swarm dynamics of charged particles in air. ²²⁵
Scattered light	* Near-infrared light scattering by lysosome-rich cells.		3T3 _x cell aggregation: lysosome-rich cells attract others by their enhanced ability to scatter near-IR light. The cells “feel” each other at distances as large as 200 μm . ²²⁶
Light-Switch Aggregation of Magnetic Colloids	* Recently observed effect – the origin of the interactions is not well understood. ^{130,131}	10 nm particles aggregate in clusters up to 100 μm	Fundamental understanding of nanoparticle interactions.

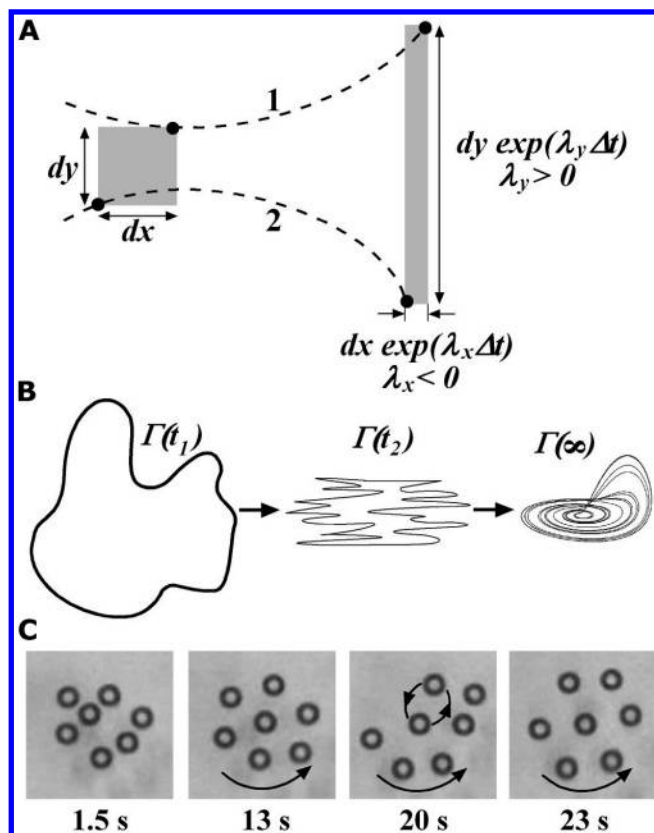


Figure 2. (A) Illustrates transformation of a two-dimensional phase space element in a dynamic system. After time interval, Δt , the distance between two points following the trajectories “1” and “2” increases in the y -direction and decreases in the x -direction. This evolution is characterized by a pair of Lyapunov exponents: positive, λ_y , and negative, λ_x . The volume of the phase-space element changes by the factor $\exp((\lambda_y + \lambda_x)\Delta t)$ and, generally, is not conserved (it decreases in the case of dissipative systems). (B) Schematic rendition of the contraction of phase space $\Gamma(t)$, occupied by a dissipative system at a given time, t . Picture on the left represents phase space at initial/equilibrium state. As the evolution progresses, the phase space volume available to the system is successively reduced (middle picture). Eventually, when the system reaches its steady state, the phase space distribution function becomes a strange attractor (right picture), whose dimension is smaller relative to that of the equilibrium state. (C) Reduction of the phase space dimensionality observed in the system of seven “spinners” in external, rotating (here, counterclockwise) magnetic field. Initially, the dimension of the phase space of N individual/independent spinners is equal to $4N$ (assuming constant angular velocity, each spinner is described by two spatial coordinates and two components of its linear velocity). The external field induces ordering of the spinners into an open lattice, which then proceeds in the counterclockwise direction. The effective dimension this lattice occupies in the phase space is close to unity and corresponds to the angular position of the lattice. Because individual spinners can randomly swap their positions (as indicated by small arrows), the rotating lattice represents a system at a strange attractor.

negative Lyapunov exponents. The positive part of the Lyapunov spectrum is, in turn, related to the entropy production in the system. The rate of entropy production per particle in the system is given by the Kolmogorov–Sinai formula,^{72,85} h_{KS} , and is calculated as a sum of the positive Lyapunov exponents, λ_i^+ , $h_{KS} = k_B \sum_i \lambda_i^+$. The Kolmogorov–Sinai entropy is a nonequilibrium counterpart of the Gibbs entropy of equilibrium statistical mechanics ($S_{Gibbs} = -k_B \ln f$) and relates the rate of information loss in the system with the flux of thermodynamic entropy, P , which is transferred to the system’s surroundings.

In a steady state, the phase space density becomes a strange attractor, whose fractal dimension⁸⁶ is less than the dimension

of the system’s phase space at equilibrium. For this reason, formation of DySA structures is accompanied by a loss in the dimensionality of the phase space (Figure 2b). Quantitatively, Kaplan and Yorke⁸⁴ conjectured that the effective fractal dimension of this attractor, D , can be expressed in terms of the Lyapunov exponents by the following formula: $D = j + \sum_i \lambda_i / \lambda_{j+1}$, with $\lambda_1 > \lambda_2 > \dots > \lambda_n$, in which j is the largest integer for which $\sum_i \lambda_i > 0$. The loss of occupied dimensionality, ΔD , relative to the equilibrium state, was observed in all dissipative systems studied so far.^{72,85} Interestingly, it has been demonstrated⁷⁷ that in the nonequilibrium heat-conducting system close to a steady state, the entropy production is proportional to product of the largest positive Lyapunov exponent, λ_{max} , and the phase space dimensionality loss, ΔD . Thus, one expects that the dimensionality of the phase space plays an important role for nonequilibrium systems and can provide the missing link between thermodynamics and statistical mechanics of dissipative systems. *In this context, we hypothesize that the sum of system’s negative Lyapunov exponents can serve as a determinant of its propensity to dynamically self-assemble, while the positive exponents can give us information on how rapidly this can happen.*

While the outlined ideas of approaching DySA through studying the properties of phase space are certainly very promising points of departure for future theories, it must be remembered that they should be treated only as preliminary hypotheses or conjectures, not theorems. The results we discussed are based on modeling alone, in which certain stringent limitations/assumptions (e.g., particle numbers only up to about one hundred, systems in which external potentials do not influence interparticle interactions⁷⁵) had to be made to make these complicated calculations feasible. We believe that future progress in this exciting field of research would be greatly facilitated if the theoretical work were accompanied by experiment. Thus, in the rest of this article, we turn our attention to practical aspects of DySA, and to the rational design of DySA systems, systems that would be both useful and would provide test beds for new theories.

4. The Practical Benefits of DySA

From an experimental/practical point of view, DySA offers several unique advantages over static SA. Structures based on DySA can exhibit adaptive/smart behaviors, can be robust in the face of large perturbations, are capable of self-healing, and can potentially self-replicate.

(i) Adaptability. Like all self-assembling systems, structures based on DySA are “smart”, in the sense that they build themselves spontaneously from well-engineered components placed in an appropriate environment.⁸⁷ DySA, however, has the added advantage of adaptability, e.g., the ability to respond to changes in the environment and to transition controllably between various modes of assembly. This adaptability is a direct result of the dynamic nature of DySA. In contrast to static assemblies, structures based on DySA live far from equilibrium and are continuously maintaining themselves. Recall that these structures represent stable (strange) attractors of the phase space and depend only on the constraints of the environment and on the imposed energy flows. Therefore, changes in the environment and/or the energy flows can modify stable structures or sometimes render them unstable, thereby leading the system to a whole new mode of assembly; in view of the concepts of nonequilibrium thermodynamics presented in the previous section, these modes of assembly correspond to different “dissipation modes.” The ability to “toggle” between stable

structures by varying environmental variables is similar to phase transitions in equilibrium systems; however, the dynamic “phases” of nonequilibrium systems are far richer and more flexible.

(ii) Self-healing. Closely related to the adaptability of DySA is its ability to self-heal.^{88–92} While structures created by DySA are surrounded in phase space by other basins of attraction, a perturbed (“wounded”) system will return (“heal”) to its stable configuration, provided that the perturbation does not bring it beyond the basin’s limits. If the perturbation is so large that the system leaves its current basin, it will evolve to a different attractor and another mode of assembly. In other words, the system will heal small wounds and will adapt to large ones. We see that adaptability and self-healing are opposing characteristics: if one would like to prepare a structure that heals from arbitrarily large wounds, this structure should be globally attracting and thus not adaptable; vice versa, if one desired to have a system that can adapt easily to small parameter changes, it would be able to heal itself only from very small wounds.

(iii) Self-replication. Finally, structures based on DySA have the potential to self-replicate. While the connection between dynamic self-assembly and self-replication has been often taken for granted (also in the previous works of one of the authors^{93–95}), one has to be rather cautious here. Let’s consider two biological examples. The first one deals with the DNA replication, in which a double-helix DNA separates, and a new complementary strand of DNA is synthesized from deoxyribonucleoside-triphosphate (dNTP) precursors self-assembling from solution onto the template strands.⁹⁶ For self-replication to occur, chemical energy must be constantly delivered to the system to (i) first unwind the DNA double helix (this is done by motor proteins called helicases, powered by hydrolysis of ATP or other nucleoside triphosphates), and (ii) “stitch” the dNTP building blocks together (this is done by polymerase complex that moves on the DNA strand by utilizing the free energy released by nucleotide polymerization). If the energy supply is terminated, the system stops self-assembling and replicating. Still, it is not a DySA system; the structures that appear after each unwinding and/or stitching event are equilibrium ones and are stable (i.e., whatever had been replicated does not fall apart in the absence of the energy flux). From a thermodynamic point of view, this system is driven from one equilibrium state to another by an appropriately engineered “agitation” (in the form of well-timed ATP or dNTP delivery and hydrolysis). Like the polymeric spheres contact-charging and assembling when shaken^{49,50} (cf. section 2 and Figure 1a (iii) and (iv)), DNA polymerization is an example of SSA driven by a nonequilibrium process/agitation.

In contrast, self-replication of cells falls into the category of DySA. To self-replicate, various pieces of cellular machinery must first self-assemble and/or migrate to appropriate locations (S phase to metaphase of mitosis).^{97,98} This requires energy, which is delivered to the cell in the form of nutrients, and is later dissipated into the environment, mostly as heat.⁹⁹ In the process of cell mitosis (from anaphase and telophase) followed by cytokinesis, microtubules and later microfilaments do mechanical work (again, this requires energy and causes heat dissipation¹⁰⁰) to separate the cell into two progenies.¹⁰¹ Importantly, these progenies are not stable states, in the sense that they require energy to maintain themselves and to potentially self-replicate again — otherwise, they will ultimately disintegrate (“die”). Overall, an ensemble of self-replicating cells

is a DySA system, since it organizes and functions only with external delivery of energy, and “falls apart” when this delivery ceases.

We emphasize that while the differences between the modes of SR discussed above might appear minute, they have important consequences for any thermodynamic theories of self-replication: While the “DNA mode” of SR (recently mimicked in artificial chemical systems^{102,103}) is treated using the tools of equilibrium thermodynamics, description of “cellular” SR must be grounded in the theory of NE systems.

5. Engineering DySA Systems: Heuristic Design Rules

The discrepancy between the versatility and creativity with which nature uses DySA and only preliminary demonstrations of DySA in man-made systems is certainly enormous. Additionally, given the absence of firm theoretical understanding and predictive tools, it does not appear reasonable to expect that DySA will be instantly developed to a level of “artificial cells”; rather, a methodical approach is needed to advance the field.

With this in mind, we adopted a bottom-up approach to DySA, in which we first try to deconstruct it into basic “engineering principles,”¹⁰⁴ use these principles to build model systems, make these systems more and more complex, study the limits of their controllability and of our understanding, and finally use the knowledge gained to fuel the theory. In this section, we formulate the “engineering principles” in the form of general, semiquantitative (“heuristic”) rules.

(i) Identifying Suitable Interactions. The first necessary condition for DySA is that at least one type of interaction acting in the system must depend on and be regulated by externally delivered energy (if the changes in energy supply would have no effect on the system’s components, it would be energetically isolated and not dissipative). The energy-dependence rule might apply to the interactions between the components of different types and/or to the global potential (e.g., an external field or boundaries of a container) acting on all of these components and keeping them together. There are two possible variations here: If the global potential is constant (e.g., hard walls confining the self-assembling pieces), then some component—component interactions must depend on the energy flow. If, on the other hand, the global potential can be manipulated by an imposed field (e.g., time dependent electric/magnetic field), the interactions between components may be independent of the energy supply. Of course, we allow a case where both the potential and interactions are energy-dependent.

There are quite a number of “dynamic” potentials and types of interactions from which DySA can be built (Tables 1 and 2). Interestingly, some of them can be designed based on phenomena that do not necessarily look dynamic, e.g., a magnetic field produced by a permanent magnet gives rise to a dynamic potential when this magnet is made to rotate.^{70,94} Moreover, some types of dynamic interactions can be set up between objects that are by themselves not responsive to external fields. One general way of achieving DySA with such components is to coat them with a layer of a responsive material/chemical. Figure 3 suggests how this idea could be used to design DySA, in which interactions are modified by the energy delivered by light. As an example, consider a collection of small particles suspended in a nonpolar solvent and whose surfaces are modified with a monolayer containing terminal azobenzene groups.¹⁰⁵ In the absence of UV irradiation, the particles’ surfaces are effectively hydrophobic, and there is no aggregation. When, however, UV is turned on, azobenzenes isomerize from a trans to a cis form, and present hydrophilic azo moieties to

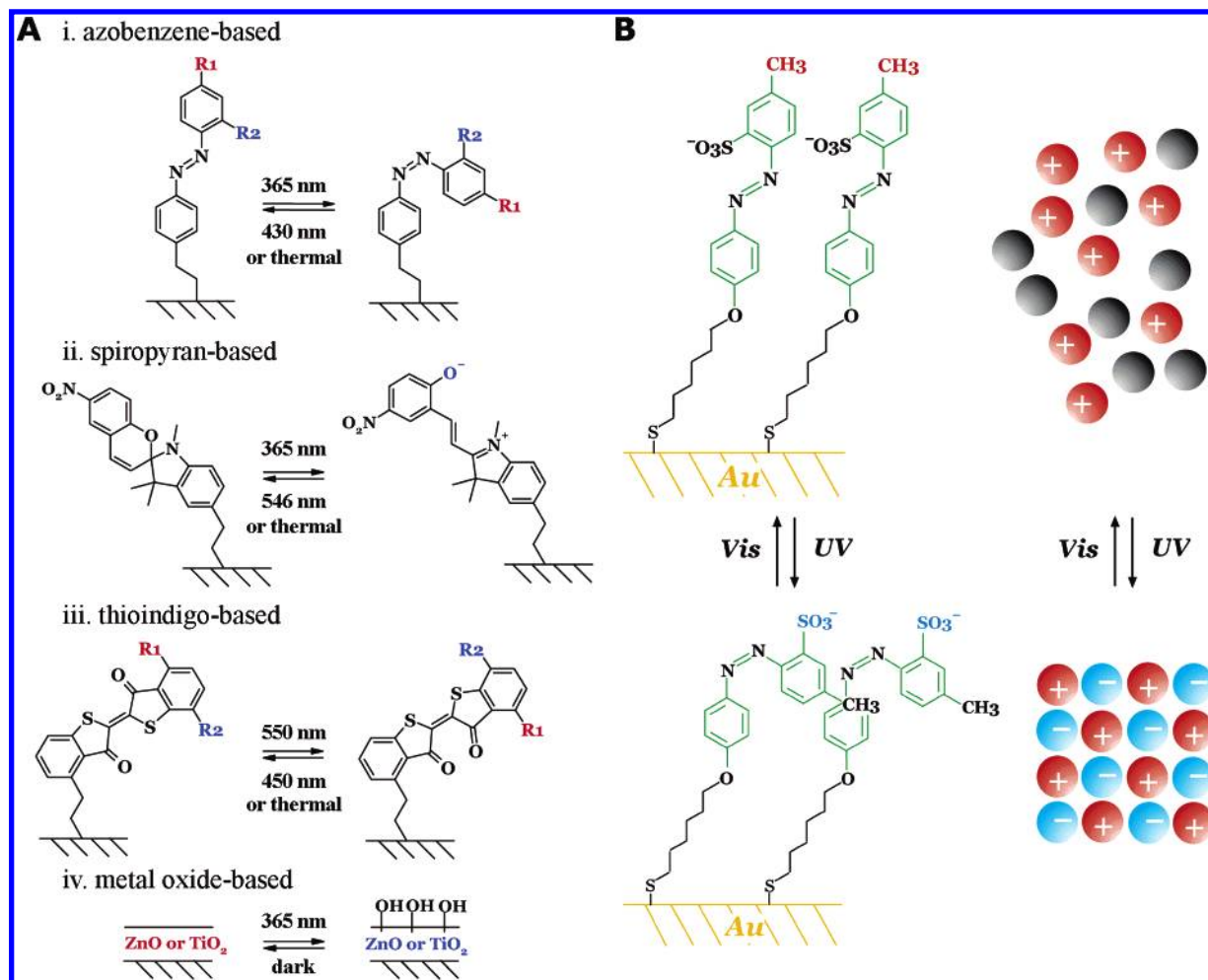


Figure 3. (A) gives examples of chemical moieties/materials suitable for creating photoswitchable surface monolayers/coatings to be used in DySA—azobenzene,¹³⁴ spiropyran,¹³⁵ thioindigo,¹³⁶ and metal oxides.^{137,138} For the organics, the isomers presented on the right are stable only upon continuous irradiation of the sample with the wavelength indicated. Spontaneous isomerization to the more stable form occurs either upon removal of this stimulus (in the dark, slow) or upon irradiation with a different wavelength specific for the given transition (fast). In addition, azobenzene and thioindigo moieties can be derivatized in a number of ways, thus creating the possibility to introduce various types of interactions (i.e., hydrophilic—hydrophobic, H-bonding, metal cation-mediated). The oxide surfaces shown in (iv), zinc oxide¹³⁷ and titanium dioxide,¹³⁸ switch from superhydrophilic to superhydrophobic upon irradiation. The process is fully reversible and removal of the UV stimulus fully restores superhydrophilicity of the surface. (B) Illustration of a hypothetical photoswitchable DySA system. Red circles denote positively charged particles (e.g., gold nanoparticles) covered with a monolayer terminated in positively charged trimethylammonium groups. Gray circles denote particles presenting switchable azobenzene units (scheme). Irradiation with UV light causes isomerization of azobenzenes so that the particles now present negatively charged sulfonate groups. This change drives self-assembly of the two types of particles. Since the azobenzenes spontaneously isomerize to the trans conformation, the assembly is stable only as long as the UV stimulus is applied.

the solvent. The now hydrophilic particles attract one another and self-assemble (cf. next paragraph). Similar switching could be achieved by thioindigo, spiropyran, or even metal oxide-based surfaces. With appropriate chemical functionalization of photoswitchable groups,¹⁰⁶ various other types of dynamic interactions can be envisioned: electrostatic (cf. example 3 in the Table), H-bonding, metal cation-mediated, etc.

Two limitations need to be considered here. First, the isomerization must be reversible in the absence of the light-stimulus or else the aggregated particles will remain in this stable state. Second, even though the switches are spontaneously reversible, the isomerization “backwards” is usually much slower than the “forward” one (e.g., picoseconds vs minutes for the azobenzene system;¹⁰⁷ nanoseconds vs seconds for the spiropyran system¹⁰⁸). To make a system assemble and disassemble dynamically, in the full sense of the word, one should speed up the backward rates; this can be done by irradiating the objects with constant-intensity light of wavelength longer (VIS) than that of periodic “forward” pulses.

(ii) **Choosing “Competing” Interactions/Potentials.** One interaction, or even one type of interaction, acting in the system is not enough to build a full-fledged DySA system. If the only forces acting between/on the components are repulsive, the system will simply fall apart; if they are all attractive, the system might dynamically aggregate (cf. previous section), but the aggregate will not develop order beyond, at best, simple closest packing. If we were to build dynamic assemblies of ordered and more complex internal structures, we must use both attractive and repulsive interactions. Only by having them “compete” with one another is it possible to introduce selectivity into the system.

(iii) **Choosing a Proper Length Scale.** To build a steady-state dynamic structure, a proper environment and a length scale must be chosen such that the opposing (attractive—repulsive) forces are similar in magnitude and can therefore balance one another. The choice of these system parameters comes from the knowledge of how the individual interactions scale with object size, its distance to other objects, and with the material

properties of the surrounding medium. Tables 1 and 2 list scaling laws for several interactions. Here, we provide a simple example of how to use them in practical design of DySA.

Suppose a two-dimensional system is to be designed, in which dielectric (polymeric), spherical particles are floating on a nonionic liquid/air interface and are subject to irradiation by UV light, which causes electrification of the spheres.¹⁰⁹ Due to the discharging processes caused by the presence of water in the air, a constant irradiation is necessary to maintain the charge generated on the spheres. In such a configuration, attractive (lateral) capillary forces would compete against repulsive forces due to charge on the particles. The attractive capillary force is given by¹¹⁰ $F_C \propto \gamma(r \sin \psi)^2 q_c K_1(q_c L)$, where r is the radius of the contact line formed around the particle, ψ is the meniscus slope at the contact line, γ is the surface tension, K_1 is the modified Bessel function of the first order, q_c is reverse the critical capillary length, $q_c = \sqrt{\rho g / \gamma}$ (where ρ is the density of the liquid and g is the acceleration due to gravity), and L is the center-to-center separation between the particles. If the radii of the spheres, R , and the distances, L , are smaller than the capillary length, the capillary force is written as $F_C \propto \gamma R^2 / L$. The repulsive electrostatic force between like-charged particles is given by $F_E \propto kQ^2 / L^2$, where k is the Coulomb constant, and Q is the charge of an individual particle. DySA can occur if the capillary and electrostatic forces are balanced and can compete. Thus, the condition $F_C \sim F_E$ sets the desired length scales at which the system should operate. Specifically, it follows from the above condition that the radii of the spheres and the characteristic distance, L^* , between them should obey the relation: $L^* R^2 = kQ^2 / \gamma$. For example, if the system is composed of particles of the radius $R = 100 \mu\text{m}$ with a charge $Q \sim 10^{-11} \text{ C}$ floating on a surface of liquid with $\gamma \sim 100 \text{ mJ/m}^2$ and $\rho \sim 1 \text{ g/cm}^3$, the characteristic distance should be of the order of $1000 \mu\text{m}$. The capillary forces are effective only if the size of the spheres and the separation between them do not exceed the critical capillary length ($q_c^{-1} = 3.2 \text{ mm}$ for the parameters considered). This condition defines an upper limit for both the radius R and the length L^* . Importantly, we note that the characteristic lengths can be modified by adjusting the properties of the particles (such as the charge, which could be dynamically modified by the intensity of the irradiation) or the properties of the fluid (e.g., density or surface tension).

(iv) Synthesis. This very general rule embodies the natural, “bottom-up” direction for developing DySA systems, from very simple systems based on a minimal number of components and types of interactions, to complex ensembles of large numbers of particles interacting in specific ways. Conceptually, this approach is akin to synthetic methods of chemistry, where one progresses from simple reactants to complex products. We advocate this methodology over the recent trend in systems’ science to analyze inherently complex assemblies/structures in a “top-down” manner. The synthetic approach offers better fundamental understanding of and ability to rationally design various levels and aspects of dynamic self-assembly.

6. DySA in Practice: Rational Design of Magnetohydrodynamic Systems

Using the rules outlined in the previous section, we, in collaboration with others, have developed a class of DySA systems based on magnetic and hydrodynamic interactions.^{46,47,70,93–95,104,111–114} Aside from illustrating the previously discussed rational progression from simple to complex, this section aims to convey two important points (i) that nature is very generous in supplying us ideas for new types of dynamic

interactions, which can sometimes be discovered by combining several known effects (here, combination of magnetically induced rotation with vortex generation gave rise to a new type of a vortex-vortex force) and (ii) that DySA systems can be relatively rapidly developed into useful devices, as illustrated by DySA fluidic machines and microfluidic mixers we describe.

(i) The Underlying Forces (Figure 4a). Consider a collection of small (tens of microns to millimeters) magnetic particles floating on top of a liquid–air interface and subject to a magnetic field produced by a permanent magnet rotating below this interface. Under the influence of the rotating magnetic field, all disks experience a centrosymmetric force F_m directed toward the axis of magnet’s rotation.⁷⁰ This magnetic force is a slowly varying, approximately linear, function of position within an interface: $F_m \sim a^3 r$, where r is the distance from the axis of rotation, and a is the radius of the particle.⁹⁴ In other words, the rotating magnetic field provides a confining dynamic potential acting on all particles. At the same time, it sets up pairwise interactions between them. This is so because the magnetic moments of the disks interact with the magnetic moment of the external rotating magnet; therefore, 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 examined using ideas from low (but not zero) Reynolds number hydrodynamics.⁷⁰ According to this analysis, the hydrodynamic repulsion F_{ij}^h 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 : $F_{ij}^h \propto \rho \omega^2 a_i^5 a_j^2 / d_{ij}^3$. The force on disk i acts along the direction of d_{ij} and away from disk j .

(ii) Dynamic Assemblies in 2D (Figure 5b–d). The interplay between attractive and repulsive interactions between the disks floating on the same interface leads to formation of ordered, open-lattice assemblies, in which spacing between the disks depends on their rotational speed, other parameters held constant. These structures can not only be decreased/increased in size by adjusting ω but can also be toggled between different spatial arrangements (Figure 5b); that is, they can transition between different basins of attraction depending on the flux of (magnetic) energy. Since the structures generated organize and live only as long as they are sustained by the external “feeding,” they fulfill all criteria of DySA.

The formation of patterns of disk-shaped spinners can be reproduced by a simple model,^{93,112} which treats the interactions between them as pairwise. Small variations to the shapes of the particles, however, can have dramatic effects not only on the magnitudes but also the nature of these interactions. One illustration of such parameter sensitivity (typical of NE systems) is illustrated in Figure 5c, which shows two modes of assembly of comma-shaped rotating plates.¹¹³ While at low and high rotational speeds the plates repel one another, at intermediate values of ω they attract and form dimers that then interact with one another repulsively. There are two interesting chemical analogies to this system. First, the formation of dimers requires that a third plate is present nearby to orient the remaining ones; in other words, the third plate catalyzes dimerization. Second, the plates can be placed onto the interface in two nonsuperimposable (i.e., chiral) positions. When rotated, only plates of one chirality dimerize, while the other “stereoisomer” is left in the form of monomers.

The chemical analogies can be further extended to the construction of assemblies that faithfully mimic the so-called, “classical artificial atoms” (in reality, structures formed by ions

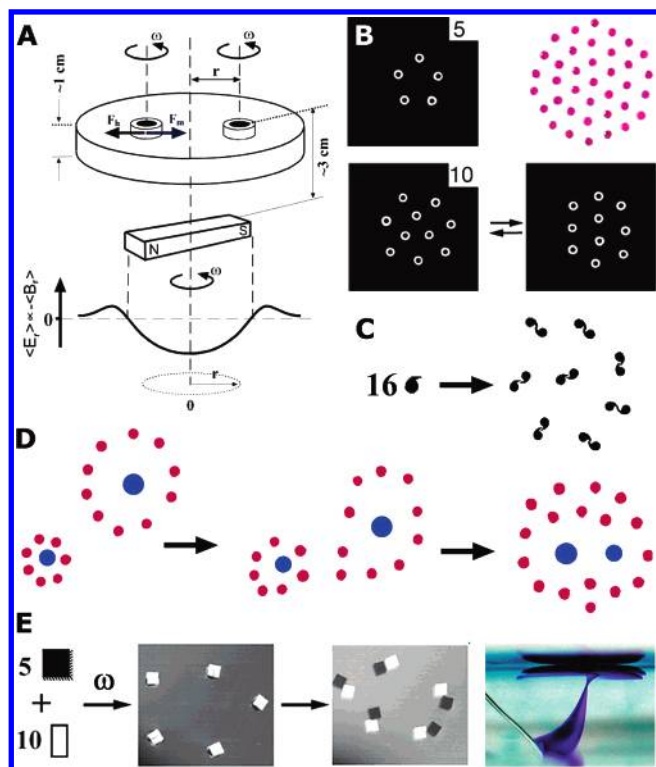


Figure 4. Magnetohydrodynamic self-assembly. (A) The simplest version of the experimental arrangement used in DySA of magnetic particles. Circular disks (0.02–2 mm in diameter) are usually made by microtransfer molding¹³⁹ from poly(dimethyl siloxane) (PDMS, Dow Corning) doped with magnetite (15–30% b/w). The disks are placed at a liquid–air interface and are fully immersed in the liquid except for their top surface. A permanent bar magnet (KIKA Labortechnik) of dimensions $L \sim 5.6 \text{ cm} \times W \sim 4 \text{ cm} \times T \sim 1 \text{ cm}$ is placed ca. 1–3 cm below the interface and rotated with angular velocity ω (200–1100 rpm). The magnet is magnetized along its longest dimension and has magnetization $M \sim 1000 \text{ G cm}^{-3}$. Magnetic force F_m attracts the disks toward the axis of rotation of the magnet. Spinning disks repel one another by pairwise hydrodynamic forces F_h . 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. (B) Dynamic patterns formed by 5 (top left), 37 (top right), and 10 (bottom) disks—10 disks can be toggled between two different arrangements. (C) Comma-shaped spinners with in-plane chirality congruent with that of the direction of the external field rotation (here, clockwise) aggregate into dimers, which then repel one another and form extended structures. Disks of opposite chirality (not shown) do not dimerize. (D) 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 toward each other. (E) Illustrates the process of pattern replication using vortex–vortex interactions. In these experiments, magnetically doped squares (black, 2 mm \times 2 mm \times 1 mm) were spinning on the PFD/EG–H₂O interface at $\omega \sim 700 \text{ rpm}$, and were used as templates to organize nonmagnetic PDMS rectangles (white, 2 mm \times 1 mm \times 1 mm) on the EG–H₂O/air interface into a pattern of squares. The rightmost picture shows a Taylor column. Interactions between such columns produced by objects rotating on different interfaces underlies self-replication in this system (for details, see ref 95). [Reprinted with permission from (A) ref 47; (B) ref 70; (C) ref 113; (D) ref 111; (E) ref 95].

subject to tight confinements^{115,116}). These “atoms” can be manipulated by modulating the profile of the external magnetic field and “reacted” with one another to give “artificial molecules” (Figure 5d).^{93,94} While these analogies are intriguing, the most important point here from the perspective of DySA is

that they illustrate a rich variety of phases and types of behaviors that can be observed in a dissipative system that is amenable to full experimental control and can be studied in quantitative detail.

Can these simple systems realize at least some promises of DySA discussed in section 4? In a primitive sense they are both adaptive and self-healing; the latter property manifests itself by the fact that when an organized structure is mechanically destroyed, it spontaneously rebuilds itself. In addition, when these systems are extended to the third dimension, they can replicate themselves.

(iii) Three Dimensions and Self-Replication (Figure 5e). Magnetohydrodynamic DySA was extended into the third dimension by layering immiscible fluids of different densities to serve as interfaces for the magnetic particles. When the particles rotated between two fluid interfaces, they generated so-called Taylor vortices,¹¹⁷ which gave rise to “vertical” forces between objects rotating on different interfaces⁹³ (cf. Table 2). These forces were repulsive at low ω and attractive at high ω , allowing switching between “staggered” and “eclipsed” lattices.

With particles of shapes more complex than cylindrical, it was possible to realize one generation of a self-replication process (Figure 5e), in which “substrate” particles present at one interface made their own copies from “templates” rotating at the other. In the particular system we studied, we used N magnetically doped squares spinning at the PFD/EG–water interface to assemble N squares of identical dimensions from $2N$ nonmagnetic rectangles floating on the upper interface. When the templates rotated, the smaller substrates were drawn toward the axes of Taylor columns created by larger templates. Once within the column, the rotating substrates created their own flow fields in the plane of the upper interface. Although these flows generated weak repulsive vortex–vortex forces acting in the plane of the upper interface on the remaining substrates, one more substrate could be drawn toward each Taylor column. When this happened, the pairs of substrates formed squares, whose strong flow fields prevented any more substrates from coming in. The process terminated when a copy of a pattern of squares from the lower interface was built at the upper interface.

(iv) Applications of Magnetohydrodynamic DySA (Figure 5). From a practical point of view, popularization of DySA would be greatly facilitated if at least some of the “theory-test-bed” systems were developed into applications. Thus, we close the discussion of magnetohydrodynamic DySA with two examples, which illustrate how this can be achieved.

The first example is that of self-assembling fluidic machines in which magnetic spinners are used to power nonmagnetic gears,^{46,114} which then self-assemble into larger structures and perform simple mechanical tasks (Figure 5a). In the absence of magnetic field, the two-component rotors are disorganized and stick together by residual capillarity. When the field is turned on, magnetic cores start rotating, and the torque they generate is transferred to the gears through the liquid between them; that is, by hydrodynamic shear. The rotors then repel one another by vortex–vortex forces and form regular open-lattice structures. When the profile of the external magnetic potential is modified by localized electromagnetic fields, the rotors can be directed to desired locations. This ability to reconfigure the rotors was used to build small machines, in which the rotors manipulated nonmagnetic containers floating at the surface of the liquid. Figure 5a shows a rotary carousel system inspired by industrial systems (normally called carousel filling and sealing machine), in which a container (in reality, a can or a bottle) is first incorporated into the carousel, moved over to a delivery point

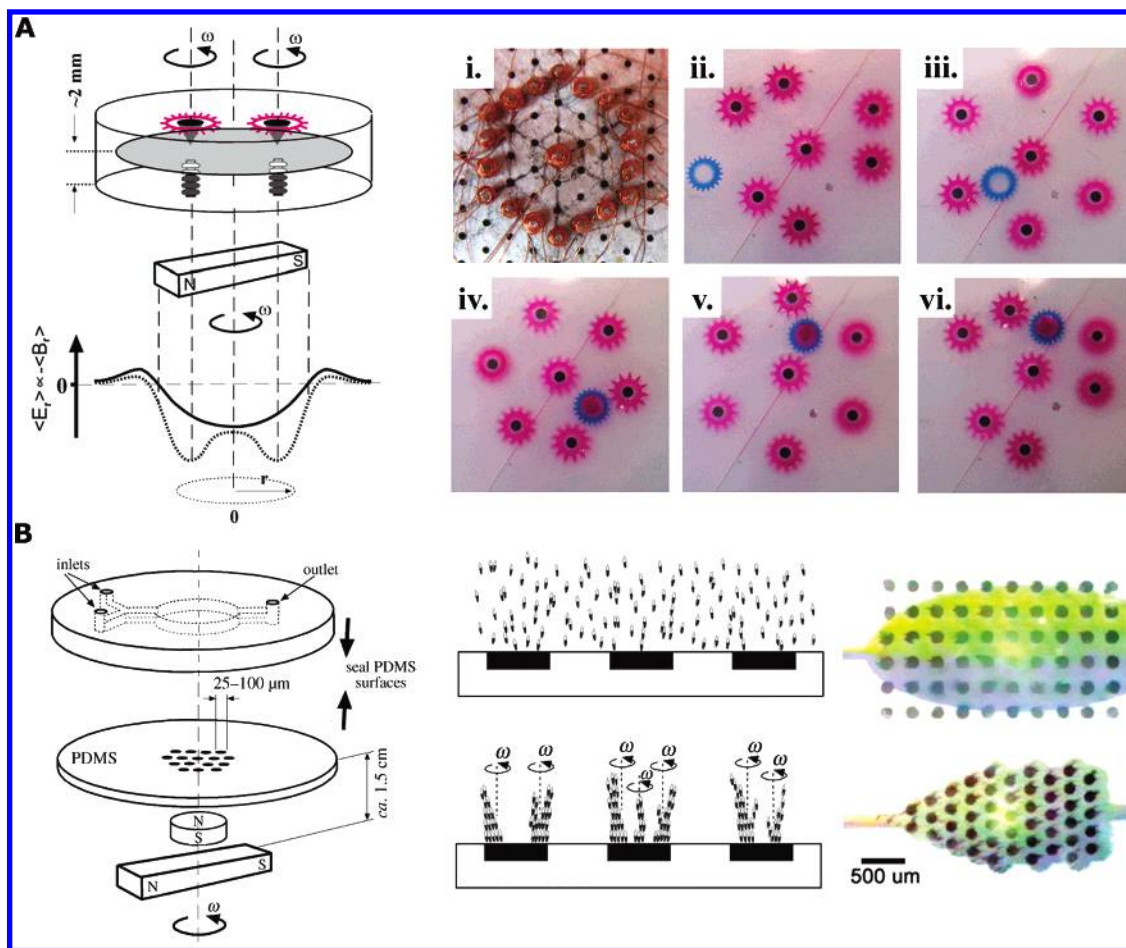


Figure 5. Applications of magnetohydrodynamic self-assembly. (A) self-assembling fluidic machines and (B) self-assembling microfluidic mixers. (A) On the left, scheme outlining the setup for self-assembling fluidic machines. The solid line in the graph is the profile of the average radial component of magnetic induction (proportional to the energy of the magnetic field) above a rotating magnet. The dotted line shows the profile of the magnetic induction along the line joining two electromagnets modifying the field of the permanent magnet. Rotors organize in the local energy minima above the electromagnets. On the right is six frames captured from a carousel system. Seven gears organize above “activated” electromagnets and are used to manipulate a nonmagnetic container 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. (B) Fabrication of a microfluidic mixer (left). In the middle, 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. On the top right, an oval micromixer operating at 100 rpm and at a flow rate of $50 \mu\text{L h}^{-1}$ is inefficient at mixing, while a more efficient pear-shaped mixer (lower right) operating at 700 rpm and at a flow rate of $50 \mu\text{L h}^{-1}$ achieves almost complete mixing. The lines on the right delineate the inlet channel. [Reprinted with permission from (A) ref 46; (B) ref 47].

where a dyed chemical is injected into it, moved further to the exit point and expelled back onto the interface. The entire manipulation is controlled by temporal changes to the external magnetic field.

The second application⁴⁷ addresses an outstanding problem of efficient mixing^{118,119} in microfluidic devices.^{120,121} While a variety of ingenious passive^{122–125} (i.e., containing no moving parts) and active^{126–128} (with moving parts) microfluidic mixers have been proposed in recent years, these devices usually require complicated/multistep fabrication procedures. In contrast, the active micromixer we developed builds itself up by the power of DySA (Figure 5b). The device consists of a sealed, microfluidic channel molded out of PDMS and having a mixing chamber whose bottom surface is patterned with small (25–100 μm in diameter) islands of magnetically doped polymer. When an external rotating magnetic field is applied to the system, these islands act as field concentrators. The mixing elements are self-assembled by simply flowing a solution of small ferromagnetic particles into the chamber. Therein, they get magnetically polarized and aggregate onto the concentrators

to form needle-like structures held together by induced magnetic dipole–dipole forces. Importantly, since the external field is a rotating one, the needles rotate with frequency, ω , equal to that of the external magnet. In doing so, the needles repel one another by vortex–vortex forces they generate in the surrounding fluid. These repulsions lead to the redistribution of the magnetic particles in such a way that all concentrators end up with needles of similar dimensions. Overall, self-assembly builds a large array of nearly identical mixing elements in a matter of seconds. As illustrated in the right portion of Figure 5b, such an array performs very efficiently in mixing streams of liquids flown laminarily into the chamber. As in all cases of DySA, the device regenerates (“heals”) itself after mechanical disruption and falls apart only when the external field is removed.

7. Summary and Outlook

We believe that the bottom-up approach exploited in the development of magnetohydrodynamic systems of increasing complexities can be applied successfully to other types of

dynamic interactions compiled in Tables 1 and 2 and in Figure 3. While some interactions/effects that might provide a basis for DySA are well understood or even widely applied (e.g., in electrorheological or magnetorheological fluids;^{68,69,129} see Table 2 for applications), others need more fundamental work to be characterized in detail (e.g., recently discovered light-induced aggregation of magnetic particles^{130,131}), and others still wait to be discovered. The effort invested in the development of DySA will very likely pay handsome dividends in the form of “smart”, adaptive, and reconfigurable materials with applications, for example, in sensors, control systems, tunable optical elements, and microdevices. The ability to manipulate many autonomous objects interacting by several types of adjustable potentials will require development of new approaches to systems’ control. Here, we envision a fruitful junction of DySA with systems’ theory and robotics. In addition, scaling down of the DySA ensembles should ultimately bring them to realm of nanoscience and even molecular chemistry. The ideas of photoswitchable dynamic crystals we suggested (cf. Figure 3) could be the first step in this direction. Finally, we stress the importance of corroborating the practical side of DySA with fundamental theoretical work on nonequilibrium thermodynamics. A theory unifying various types of dissipative systems would not only be relevant to DySA but would ultimately bring us closer to the understanding of life.

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