Switchable Static and Dynamic Self-Assembly of Magnetic Droplets on Superhydrophobic Surfaces

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Self-assembly is a process in which interacting bodies are autonomously driven into ordered structures. Static structures such as crystals often form through simple energy minimization, whereas dynamic ones require continuous energy input to grow and sustain. Dynamic systems are ubiquitous in nature and biology but have proven challenging to understand and engineer. Here, we bridge the gap from static to dynamic self-assembly by introducing a model system based on ferrofluid droplets on superhydrophobic surfaces. The droplets self-assemble under a static external magnetic field into simple patterns that can be switched to complicated dynamic dissipative structures by applying a time-varying magnetic field. The transition between the static and dynamic patterns involves kinetic trapping and shows complexity that can be directly visualized.

References and Notes


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Supplementary Materials

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Materials and Methods

Supplementary Text

Figs. S1 to S9

Table S1

References (27–40)

Movies S1 to S18
but seminal works have shown that it can also be created artificially (12, 13, 17).

Dynamic self-assembly has been suggested as a route to adaptive systems beyond what static self-assembly can offer (2, 13, 18). However, dynamic assembly is challenging to realize and understand because it cannot be predicted through energy minimization. It is also sensitive to small, local changes in the interactions between the elementary units and the external energy supply (13). We approach this problem by introducing a model system that functions in the interface of static and dynamic self-assembly and can be switched between them. The system relies on manipulation of mobile magnetic ferrofluid droplets (19–21) on a low-friction lotus-leaf-like (22) superhydrophobic surface (23–27) with an external magnetic field. In the following text, we first show how an external magnetic trigger can be used for creating self-assembled ferrofluid droplet populations from a single parent droplet. Then, we demonstrate that the static equilibrium patterns can be transformed reversibly to dynamic dissipative patterns by feeding them energy through kinetic trapping. P1; high magnetic field; P2, low magnetic field. Error bars indicate SD of three data sets. (D) Scheme of controlling the lattice constant in the kinetically trapped patterns by adjusting the magnetic field curvature (c) and the magnetic moment of the droplets (m). a, nearest-neighbor distance. (E) Snapshots of a 19-droplet pattern with two extreme periodicities at high and low magnetic fields. (F) The corresponding nearest-neighbor distance as a function of $\sqrt{m/c}$. Red dots denote experimental measurements; the black line indicates the best linear fit.
an oscillating magnetic field. We highlight the important role of kinetic trapping as a stabilizer on both static and dynamic patterns and directly visualize the complexity of the transition.

In an elementary experiment, one droplet of aqueous ferrofluid (Fig. S1) (28) is placed on a superhydrophobic surface and subjected to a confining field of a cylindrical permanent magnet below the substrate (Fig. 1A and fig. S2). Gradually increasing the field strength \( H \) and the vertical gradient \( dH/dz \) acting on the droplet (by decreasing the gap between the magnet and the surface) leads to a deformation of the droplet into a spiked cone and cleavage into two smaller droplets at the critical field strength (Fig. 1B and movie S1). The division takes a few tens of milliseconds (Fig. 1C and movie S2), after which the daughter droplets briefly oscillate before settling at their equilibrium separation (Fig. 1D).

The division of the droplet is due to a combination of high magnetic field and high vertical magnetic field gradient and, therefore, does not take place in a homogeneous magnetic field (fig. S4). The division is related to the normal-field instability of ferrofluids (Rosensweig instability) (19), but differs from it in several ways. The classic Rosensweig pattern [see (29) for a demonstration] appears in a homogeneous perpendicular magnetic field on a horizontal flat surface of ferrofluid. It has the critical periodicity of \( \lambda_{c, \text{Rosensweig}} = 2\pi \sqrt{\sigma/\rho g} \), where \( \sigma \) and \( \rho \) are surface tension and density of the fluid, respectively, and \( g \) is the gravitational acceleration (30). In contrast, the gravitational force in our system is negligible compared with the magnetic force due to the vertical field gradient; that is, \( \frac{\mu_0}{2} \langle \mu H M \rangle \), where \( \mu_0 \) is permeability of vacuum, \( M \) is magnetization, and \( V \) is volume of the droplet. This magnetic force can be up to two orders of magnitude larger than the gravitational force (fig. S5).

Thus, we can approximate the critical wavelength in our system as

\[
\lambda_c \approx 2\pi \sqrt{\frac{\sigma}{\mu_0 H V}}
\]

Importantly, Eq. 1 has a different interpretation compared with the Rosensweig pattern. In this case, Eq. 1 does not determine the periodicity of the pattern but instead gives the criterion for the splitting: a droplet divides when the critical wavelength becomes smaller than the droplet diameter. This implies that the largest droplet is always the most susceptible to dividing (Fig. 2A), which is a sum of the dipolar repulsion between the magnetized droplets and their attraction toward the increasing gradient of the external magnetic field.

The droplet pattern quickly rearranges to accommodate the newly formed droplet after each division (Fig. 2B and movie S3). The rearrangement is driven by the minimization of energy, which is a sum of the dipolar repulsion between the magnetized droplets and their attraction toward the increasing gradient of the external magnetic field.

\[
U = \frac{\mu_0}{4\pi} \sum_{j=1}^{N} \sum_{i=1}^{N} \frac{m_i m_j}{|r_i - r_j|^3} = \mu_0 \sum_{j=1}^{N} m_j \left( H - \frac{1}{2} c |r_j|^2 \right)
\]

where \( m_i \) and \( m_j \) are magnetic moments of the droplets; \( r_i \) and \( r_j \) are positions of the droplets; and \( c = -\frac{\mu_0 H}{\sigma} \) is the confining curvature of the
magnetic field (fig. S2). The rearrangement after each division is nearly perfect due to the low friction that originates from the surface’s high contact angles and low contact angle hysteresis. In contrast, other surfaces with higher contact angle hysteresis did not allow the minimum energy patterns to be reached (movie S4).

The lattice constant of the patterns could be adjusted by changing the ratio between the repulsion and attraction by changing the distance between the surface and the magnet (Fig. 2, D to F), in good agreement with the scaling relation for the nearest-neighbor distance $a \propto \sqrt{m/c}$ predicted from Eq. 2. Importantly, the periodicity changes are completely reversible (provided that the field is not increased above the next division threshold). Thus, the droplets are free to move, despite the number of droplets being kinetically trapped (Fig. 2C).

More complicated patterns are readily achieved by using other magnetic field geometries, such as that of a nonaxisymmetric rectangular cuboid magnet (Fig. 3A). The lacking axial symmetry changes the typical five- and sixfold patterns observed with cylindrical magnets (Fig. 3B) to close-packed ribbons with an overall twofold symmetry (Fig. 3C and movie S5). On the other hand, starting with multiple differently sized parent droplets (Fig. 3D) makes switching between hierarchical patterns possible (Fig. 3E, fig. S7, and movie S6).

The static patterns transform to dynamic ones when they are provided with a sufficient continuous energy feed to keep them away from the energy minimum (Fig. 4A). We realized the energy feed by oscillating the permanent magnet horizontally below the substrate with amplitude $A$ and frequency $f$ (Fig. 4B). At low energy feed rates (small amplitude and frequency), a typical static seven-droplet pattern simply moves with the oscillating magnet as a whole and, thus, remains close to the energy minimum (Fig. 4, C and D, mode I, and movie S7). However, the droplets start to coalesce above a threshold amplitude and frequency, leading to the emergence of numerous dynamic patterns consisting of elongated droplets and/or regular circular droplets (Fig. 4, D and E, modes II to X, and movies S7 and S8). The transition threshold is determined by the time-dependent dissipative magnetic forces, which cause shortening in the distances between the droplets (Fig. S8). Thus, the dynamic magnetic force is an external trigger that can free the static pattern from its kinetic trap (Fig. 2C). It allows the number and sizes of the droplets to be changed, leading to the rearrangement of the pattern.

Simulations showed that the coalescence and rearrangement starts from droplet pairs whose distance is affected the most by the energy feed (Fig. 4F and fig. S8). However, immediately after the first coalescence, the behavior of the pattern becomes difficult to predict, as seen from the complex and seemingly chaotic coalescence and division of droplets (movie S8, mode IX). This complexity originates mostly from small differences in initial positions and sizes of the droplets (fig. S6). However, complexity can arise, even in individually pipetted droplet patterns (movie S10), and is actually seen also in switching of some static patterns (fig. S9 and movie S11). Yet, even the most chaotic transient droplet motions eventually stabilize into kinetically trapped patterns that are permanent until the oscillating field is switched off, after which the

![Fig. 4. Reversible switching between static and dynamic self-assembly. (A) Scheme of the switching. (B) Practical realization of the energy feed by horizontally oscillating the permanent magnet below the superhydrophobic surface. (C) Phase diagram of the seven-droplet pattern in the field of 1130 Oe ($dH/dz$ 132 Oe/mm), showing the transition boundary (dashed lines). (D) Scheme of mode I and photographs of dynamic patterns that do not change their appearance during the cycle of the driving field (movie S7). (E) Scheme of mode VI and photographs of dynamic patterns that change their shape (but not the number of droplets) periodically with the external magnetic field (movie S8). (F) Photographs of the intermediate steps in the formation of mode VIII during 2.5 oscillations of the driving field ($f = 3$ Hz, $A = 12.5$ mm) (movie S9).](http://science.sciencemag.org/)
patterns decay back to the static seven-droplet pattern within a fraction of a second.

Dynamic patterns rely critically on low friction and energy dissipation (movie S12). The geometry of the dynamic patterns cannot be described in terms of energy minimization (Eq. 2), because they are far from the energy minimum. Instead, the patterns are better described and rationalized as dynamic states wherein the droplet number is kinetically trapped [as in the static patterns (Fig. 2C)]. Patterns can be classified into those that alternate (Fig. 4E) or do not alternate (Fig. 4D) during the cycled energy feed. Alternation is caused by different mobilities of the droplets: Elongated ones are more mobile because of the higher ratio between the driving and dissipative forces.

Dynamic self-assembly can be used as a switch between droplet patterns with different numbers of droplets. In contrast to the division instability, dynamic self-assembly decreases the number of droplets. This allows the irreversibility of the droplet formation in static self-assembly (Fig. 2C) to be overcome. For example, driving any static pattern to the mode V dynamic pattern (single elongated droplet) and decreasing the magnetic field while oscillating the magnet allows recovery of the original one-droplet state (movie S13). This is the final unit operation required to realize a complete cycle from a single liquid droplet to complicated static and dynamic patterns and, finally, back to the starting state (fig. S10). Externally driven magnetic droplets on superhydrophobic surfaces form a versatile model system for studying and visualizing complicated phenomena in self-assembly. We used this model to demonstrate switching between static and dynamic self-assembly and to show the usefulness of kinetic trapping that most often is viewed only as a hindrance for assembly. The most diverse patterns were found to occur near the boundary where static patterns switch to dynamic ones. The transition is complex, and its detailed investigations will pave the way toward a better understanding of the onset of dynamic dissipative self-assembly.

References and Notes


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Supplementary Materials

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Supplementary Text

Figs. S1 to S10 References (31–35)
Movies S1 to S14
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Ultrahigh Magnetoresistance at Room Temperature in Molecular Wires

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Systems featuring large magnetoresistance (MR) at room temperature and in small magnetic fields are attractive owing to their potential for applications in magnetic field sensing and data storage. Usually, the magnetic properties of materials are exploited to achieve large MR effects. Here, we report on an exceptionally large (>2000%), room-temperature, small-field (a few millitesla) MR effect in one-dimensional, nonmagnetic systems formed by molecular wires embedded in a zeolite host crystal. This ultrahigh MR effect is ascribed to spin blockade in one-dimensional electron transport. Its generic nature offers very good perspectives to exploit the effect in a wide range of low-dimensional systems.

In spintronic devices, the electron’s spin is exploited for information processing. Typically, these devices contain layered structures with an electrical resistance that is dependent on the relative orientation of the magnetization of their magnetic layers; thus, the resistance can be altered by an external magnetic field, a phenomenon called magnetoresistance (MR). Examples include giant magnetoresistance (GMR) devices (1, 2), which are multilayer stacks of ferromagnetic materials separated by a nonmagnetic metal spacer layer, and tunnel magnetoresistance (TMR) devices (3, 4), which have a tunnel barrier as the spacer. Here, we explore entirely different physics in a nonmagnetic system, relying on a mechanism akin to spin blockade in quantum devices.

The Pauli principle precludes that an electron can tunnel into a state already occupied by another electron with the same spin. This spin blockade for two electrons starting from a spin-triplet configuration was first observed in quantum dots (QDs) at cryogenic temperatures (5). Spin blockade can be lifted by spin relaxation, mixing in singlet character. It has been shown that hyperfine interaction can lift spin blockade in QDs (6). The importance of hyperfine interaction on spin dynamics has also been recognized in the context of an intrinsic, room-temperature MR effect in organic semiconductors (7, 8). Carrier transport is influenced by spin-dependent reactions, which are subject to the competition between an external magnetic field B and the random hyperfine fields BHF (~1 mT) of the nuclei. At small B (Fig. 1A), hyperfine interactions

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Editor's Summary

Magnetic Self-Assembly

During self-assembly, objects spontaneously assemble into larger ordered patterns as observed, for example, in the phase segregation of block copolymers or the assembly of micrometer-sized objects and components in electronics. In dynamic self-assembly, the ordered patterns require an external energy source, but still form because of intrinsic interactions within the system. Timonen et al. (p. 253; see the Perspective by Hermans et al.) studied the organization of magnetic droplets, in the form of a ferrofluid, placed on a low-friction surface. A time-varying magnetic field transformed the statically arranged droplets into a dynamic pattern.