Three-dimensional self-assembly using dipolar interaction

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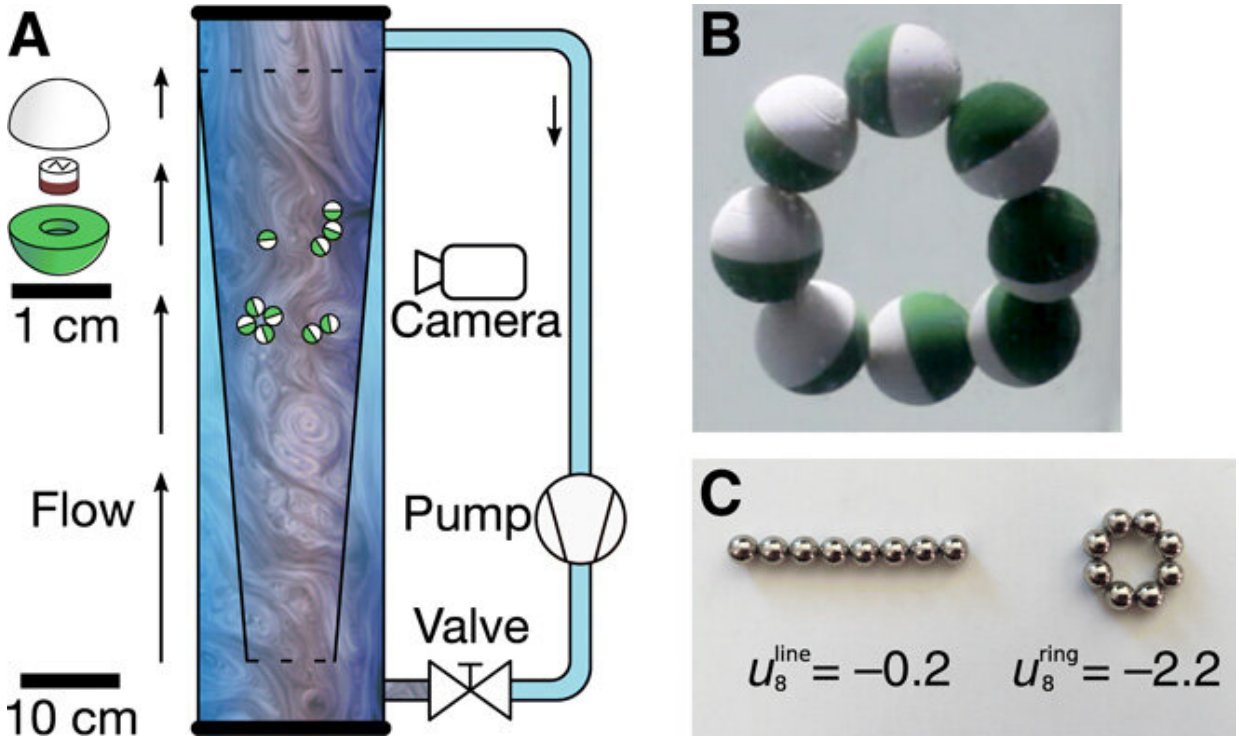


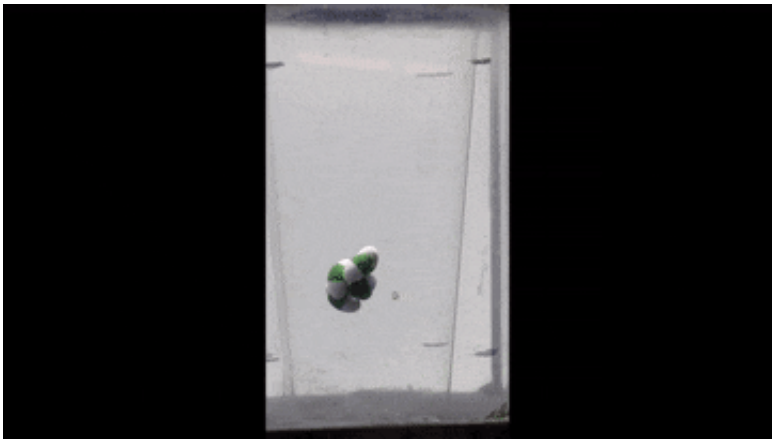
The self-assembly experiment. (A) 3D printed polymer objects with embedded permanent magnets were inserted in a transparent cylinder with an upward flow. The flow counteracts the drop velocity of the objects, and the flow's turbulence provides a disturbing force. A tapered transparent insert was used to provide a gradient in the flow velocity, which ensured that the objects levitate in front of the video cameras. (B) Spherical objects form linear chains. When eight spheres are inserted in the flow, the most stable configuration is a circle, which has 10% lower energy than a linear chain (C). Photo credit: L. Abelmann (Saarland University and University of Twente). Credit: Science Advances, doi: 10.1126/sciadv.aba2007

In materials science, interactions between dipolar forces of permanent magnets can lead to form one-dimensional chains and rings. In a new report on *Science Advances*, Leon Abelmann and a research team in electronic components, technology and materials at the Saarland University, University of Twente and Delft University of Technology in Germany and Netherlands investigated the possibility of allowing dipoles to self-assemble into 3-D structures by encapsulating them in a shell of a specific shape. The team realized the conditions for such self-assembly in a 3-D crystal when the dipole energies in parallel and anti-parallel states were equal. They formed the most regular structures using cylinders and cuboids, and the simple design rule helped form 3-D crystals from objects in the micron range, opening the way to engineer hitherto unknown metamaterials.

Crystal growth is a version of self-assembly in which individual objects can be arranged into regular arrays with broad technical impact, ranging from silicon single crystals to diffraction studies on proteins. The process of crystal growth begins with nucleation, starting on well-defined templates or on random imperfections, or spontaneously in space. The team focused on the latter mechanism of formation in this work. The formation of crystals at the macroscale (beyond atoms and molecules) is presently receiving increased attention due to its promise to form metamaterials with novel functionalities. Researchers had previously observed intricate crystal growth from silica or polymer spheres including photonic crystals. Such processes relied on solvent evaporation to bring components in to each other's vicinity, assisted by solvent flow, although the process can also be driven by sedimentation – leading to close-packed structures.

In this work, Abelmann et al. studied the possibility of self-assembling crystals under permanent magnetic dipolar forces. The team conducted

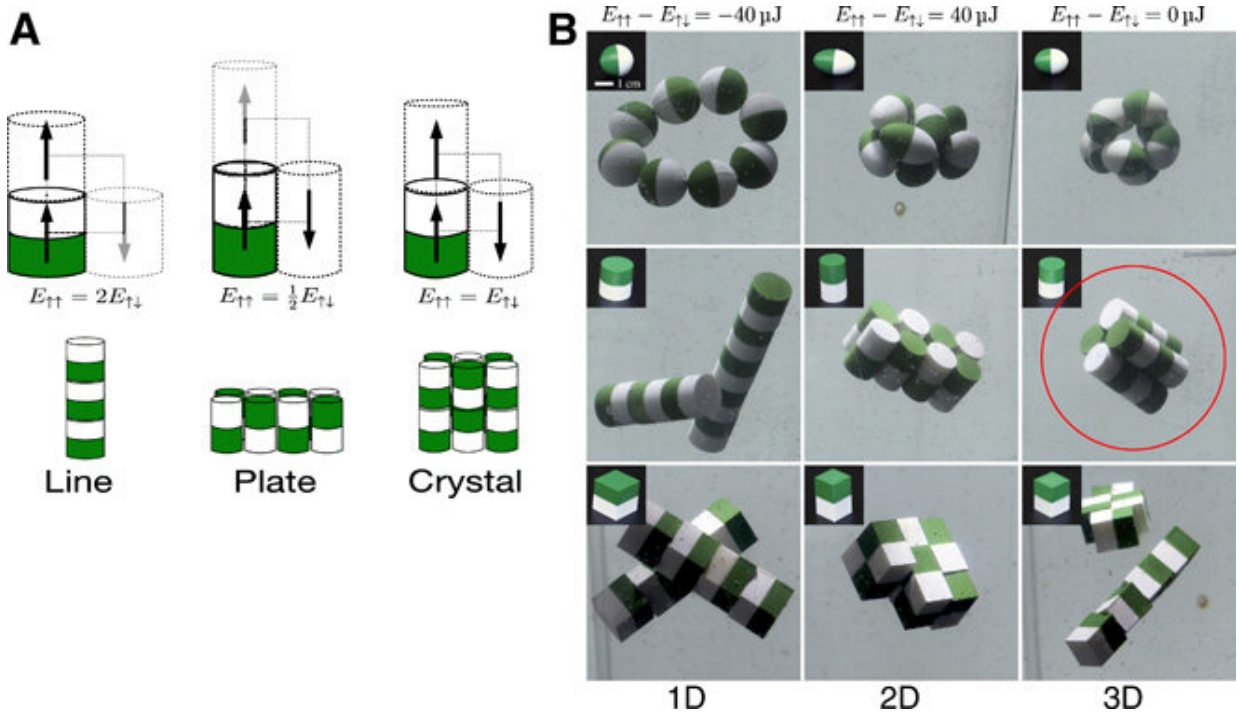
experiments with millimetre-sized permanent magnets embedded in a polymer shell of varying shapes. They then submerged the object in water and counter-balanced the gravitational forces with an upward water flow to maintain objects in the field of view of the camera. The adjustable turbulence in the flow created disturbing forces to provide stochastic kinetic energy to objects, similar to Brownian motion. Interactions between the permanent spherical dipoles resulted in the formation of chains, and eight dipoles could assemble to form a ring, in a well-understood mechanism. The dipolar forces first organized spheres into a line, and with more than three spheres the team observed the system reach a lower energy state to close the line into a ring. They noted substantial energy gain in the case of eight spheres, allowing the rings to form easily and remain intact.



Video recording of eight spheroids, cylinders, and spheroids with three different aspect ratios. For full video see Credit: Science Advances, doi: 10.1126/sciadv.aba2007

Abelmann et al. used the shape of the polymer shell to change the distance between dipoles for diverse orientations. The scientists elongated the shell to increase the distance between dipole centers to

obtain 2-D plate-like structures. If the energies between the parallel and anti-parallel states were equal, the newly arriving dipoles aligned similarly to form 3-D structures. The team demonstrated the strategy to form eight spheroids, cylinders and cuboids and chose an energy difference of 40 μJ for the antiparallel and parallel states for all shapes. When they reversed the energy difference between the parallel and antiparallel states, so that the antiparallel state demonstrated the lower energy, they noted clear plate structures for cylinders and irregular structures for spheroids. However, when both energies were equal, Abelmann et al. observed the cylinders to form 3-D clusters. Therefore, provided there was no preference for parallel or antiparallel alignment, the experimental setup could self-assemble 3-D structures based on dipolar forces. Furthermore, relatively stable attachments of the cuboid assemblies led to magnetic flux closure that prohibited further growth, while spheroids formed complex double-ring structures resembling those predicted in previous simulations.



3-D self-assembly of dipoles. (A) Equally spaced dipoles prefer parallel alignment (black arrows). By elongating the shape of the shell around the dipoles, we can favor the antiparallel configuration, so that plates of objects assemble. When the energy of the parallel and antiparallel configuration is exactly equal, we expect 3D crystals. (B) This strategy works best with cylindrical objects. From left to right, we varied the shape so that the energy of the parallel configuration is twice (left), half (center), and exactly equal (right) to that of the antiparallel configuration. The red encircled assembly of cylinders (middle row) is a regular 3D 2 by 2 by 2 cluster. The cylindrical objects in the second row reproduced the plate prediction of (A). The spheroids (top row) and the cubes (bottom row) exhibited line structures in the first column but more complex behavior when their shape was adjusted. Credit: Science Advances, doi: 10.1126/sciadv.aba2007

The structure of spheroids also stayed together for several minutes, much longer than cylinders and cubes that disintegrated into parts after a few seconds. For instance, during the experiments, the ring structure of spheres broke apart to form a chain but then reconnected into a ring in less than a minute. Abelmann et al. credited the higher stability of spheroid structures to their ability to misalign without immediately increasing their distance—thereby decreasing the force between the magnets. Chain structures broke more easily due to single bonds compared to plates or crystals with multiple bonds. Cylinders and cubes could also assemble to form long rigid chains that broke off on frequent contact with the reactor walls.

Based on the shapes investigated in the study, cylinders appeared best-suited to self-assemble into well-defined 3-D structures since additional experiments showed that spheroids did not comparatively self-assemble to form regular crystals. Clusters of cylinders and cuboids could break into smaller clusters then realign to form more regular crystals. Disintegration of larger assemblies occurred more frequently due to

increased shear forces. The effect may also be amplified by the energy in the turbulent flow, although it is not known if the effect was typical for turbulent driven self-assembly or induced by other experimental factors. Abelmann et al. intend to find answers by studying the phenomenon further by changing the absolute size of objects.

Video recording of spheroids, cylinders, and spheroids with balanced energy for the parallel and anti-parallel alignment, with 8, 12, and 16 objects. Credit: Science Advances, doi: 10.1126/sciadv.aba2007

In this way, Leon Abelmann and colleagues experimentally demonstrated the capacity for 3-D structures to self-assemble from dipolar forces, provided there was no preference for parallel or antiparallel alignment. The scientists achieved this by balancing dipolar forces via steric interactions induced by the specific shape of the object. They selected

the cylindrical shape as it appeared to be a good compromise to help achieve regular crystals. The experiments also agreed with molecular dynamics simulations where spherical shapes were more likely to form large clusters than cubes, while dipolar interactions disturbed crystal formation of cubes.

The results encourage experiments on crystal self-assembly at the microscale using permanent magnetic dipoles. Based on the results, materials scientists will be able to envision exciting metamaterials such as artificial antiferromagnets, piezomagnetic materials and 3-D magnetic ring-core memories. The force between dipoles did not change relative to the size of the dipoles, while their origin as magnetic or electric dipoles had no experimental effect, therefore Abelmann et al. intend to generalize the experimental outcomes for 3-D assembly at the micron scale. The outcomes will lead to the formation of photonic crystals, supermaterials, 3-D electronics or memories.

More information: Leon Abelmann et al. Three-dimensional self-assembly using dipolar interaction, *Science Advances* (2020). DOI: 10.1126/sciadv.aba2007

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