Arranging matter by magnetic nanoparticle assemblers

Benjamin B. Yellen^{*†}, Ondrej Hovorka[‡], and Gary Friedman^{*}

^{*}Department of Mechanical Engineering and Materials Science, Duke University, Box 90300 Hudson Hall, Durham, NC 27708; and [‡]Department of Electrical and Computer Engineering, Drexel University, 3141 Chestnut Street, Philadelphia, PA 19104

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We introduce a method for transporting colloidal particles, large molecules, cells, and other materials across surfaces and for assembling them into highly regular patterns. In this method, nonmagnetic materials are manipulated by a fluid dispersion of magnetic nanoparticles. Manipulation of materials is guided by a program of magnetic information stored in a substrate. Dynamic control over the motion of nonmagnetic particles can be achieved by reprogramming the substrate magnetization on the fly. The unexpectedly large degree of control over particle motion can be used to manipulate large ensembles of particles in parallel, potentially with local control over particle trajectory.

colloidal | manipulation | self-assembly | tweezing | transport

Optical (1, 2) and electrical fields (3, 4) have been used to transport, sort, and assemble microscopic objects, such as colloidal particles, cells, and molecules above surfaces. These techniques are certainly appealing for fabricating an emerging paradigm of devices (5–8), yet neither technique has demonstrated sufficient flexibility required for widespread adoption. Optical manipulation is based on trapping particles in regions of high optical field intensity (9). Fast scanning of optical beams has been successful in manipulating colloidal particles over a relatively small area (10); however, optical trapping over large areas requires the task of generating holographic maps (11), which are difficult to reconfigure. Electric field manipulation is based on trapping particles in the minima or maxima regions of electric field intensity, which can be accomplished by applying ac electric field to arrays of electrodes at various frequencies (12, 13). However, programmable electrical trapping requires sacrificing portions of the substrate for complex wiring patterns and logic for addressing individual electrodes in the array. By contrast, the ability of ferromagnetic materials to store magnetic information without any external power makes it an optimal medium for programming highly dense information over large areas of a substrate. This nonvolatility is precisely the reason why magnetic recording is the preferred data storage technology for large computer information systems. The same benefits can be extended to program the assembly and manipulation of colloidal materials above a substrate. Optical or electric field manipulation techniques may have other undesirable effects, particularly for biological materials and living cells. For example, optical fields can cause significant heating, whereas intense electric fields can interfere with various biochemical and biological processes. Magnetic fields, in contrast, have practically no effect on living systems.

Magnetization patterns, originally used for data storage, are used here to control assembly and transport of nonmagnetic particles ranging in size from <100 nm to several micrometers. Magnetic forces on nonmagnetic particles are transmitted through a fluid dispersion of magnetic nanoparticles, such as commercially available ferrofluid. Previously, magnetic forces have been exploited to assemble nonmagnetic particles into somewhat regular structures within the bulk of the fluid, but little control over the assembly process was achieved (14, 15). In the present work, we employ magnetization patterns as a tem-

plate for producing reprogrammable magnetic field maps, which leads to improved control over particle assembly and manipulation. Instead of creating magnetization patterns in uniform ferromagnetic films through magnetic domain patterning, we chose to create these patterns by lithographically patterning ferromagnetic thin film into discrete patches. These patches are used as reprogrammable (i.e., remagnetizable) magnetic traps for manipulating colloidal particles in a highly flexible manner. Whereas control over particle trajectory with local precision can be achieved by magnetizing individual traps in the array, global synchronization of particle motion can be accomplished by applying uniform pulsating or rotating magnetic field to the entire system. It should be stressed that the main purpose of the work reported here is to establish the underlying physical principles, investigate the relative importance of various effects, and demonstrate the large degree of control over nonmagnetic colloidal objects that can be achieved through magnetic forces. For this reason, we restrict our attention to systems where all of the magnetic traps are magnetized in the same direction at any given time, even though the possibility of programming individual traps independently from each other does exist and can be accomplished by optically addressable thermomagnetic recording technology (16).

The rest of the work is organized as follows. First, the basic principles guiding particle transport and assembly will be discussed briefly. Next, the large-scale assembly of colloidal particles onto magnetic trap arrays will be empirically demonstrated, and the conditions for optimal particle assembly will be noted. Then, the ability to transport colloidal particles across an open substrate will be demonstrated. Finally, the ability to sort ensembles of particles on a substrate by using discontinuities in magnetization patterns will be demonstrated. Sorting experiments will be used to support the claim that ensembles of particles can be transported and assembled, potentially with individualized control if the magnetic trap array is programmed through conventional magnetic recording techniques. Potential applications of these techniques and major open questions will be noted in *Conclusion*.

Materials and Methods

Experimental work used 70-nm-thick cobalt film patterned into different shapes, period distances, and geometrical arrangements on silicon or glass wafers. The film was produced by traditional metal evaporation and lift-off techniques as described in ref. 17. The saturation magnetization of the patterned micromagnets was ≈ 1 tesla, in accordance with previously reported properties of patterned 50-nm-thick cobalt film (18). Some of the micromagnets used in the experiments have planar dimensions of $3 \times 12 \mu\text{m}$. However, all of the work involving quantitative measurements used $5\text{-}\mu\text{m}$ circular micromagnets

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[†]To whom correspondence should be addressed. E-mail: yellen@duke.edu.

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Fig. 1. Bead levitation and microtweezing by magnetic traps. In the absence of external magnetic field, latex beads (red spheres) are stably levitated above the surface as illustrated in *a* due to repulsion by the magnetic nanoparticles in the fluid (brown dots). When the external field is activated, the particles are attracted to different positions on the traps, depending on the orientation of the field (blue arrow) with respect to trap magnetization (white arrow). The bead is initially attracted to the left end of the trap in *c*, and after successive magnetic field rotations, the bead moves from the left end to on top of the trap, then to the right end of the trap, and finally in between traps. In *c*, a quasi-static transport model for bead movement in rotating magnetic field is demonstrated. Provided in *b* is experimental demonstration of 3- μm latex beads (Duke Scientific) assembling onto 5- μm magnetic traps in the influence of static applied magnetic field. (Scale bar: 25 μm .)

arrayed in either hexagonal or rectangular formations. The array spacing (distance from one trap to the next) was 8 μm for both rectangular and hexagonal arrays. The symmetry in arrays of circular micromagnets made them the simplest object of study.

Magnetic nanoparticles of $\approx 100\text{-}\text{\AA}$ diameter were purchased from FerroTec (Nashua, NH) in aqueous-based solution (i.e., ferrofluid) with particle content occupying 1.1% vol fraction of the fluid. The ferrofluid had initial magnetic susceptibility of 0.24 and a viscosity of 0.05 poise. Monodisperse nonmagnetic colloidal particles were purchased from Duke Scientific (Palo Alto, CA) in aqueous-based solution with particle content occupying 1% vol fraction of the fluid. The particles expressed a fluorescent signal in either the red or green spectrum so that their movements could be observed by fluorescent microscopy. The fluorescent particles were purchased in various sizes, with diameters ranging from 90 nm to 5 μm . The purchased particles were sterically and electrostatically stabilized; however, some aggregation of the particles inside the ferrofluid was observed. The ferrofluid/particle mixture was placed directly on the wafer surface, and the fluorescent particles were moved about the surfaces by externally pulsating or rotating magnetic field.

The rotating magnetic field was produced by using several orthogonal sets of solenoid coils with iron cores arranged with respect to the wafer. The arrangement of coils was designed to ensure control over the magnetic field in three orthogonal directions (i.e., the x -, y -, and z -directions). Reasonably uniform magnetic fields in the range of 0–200 G in any direction could be applied with this setup. The magnetic field was measured with a hand-held Hall probe, purchased from Lake Shore Cryotronics (Westerville, NY). Each set of coils was connected to an independent channel, and their waveforms were programmed in DASLAB 7.0 software to produce controlled magnetic field rotation.

The assembly process was observed with a Leica DM LFS microscope through an air immersion lens. The microscope was adjusted for phase contrast to best observe the bead/ferrofluid contrast on the wafer surface. To visualize the assembly process,

a glass slide was placed on top of the drop to create a semi-transparent thin film that could be observed through the microscope. In some cases, a spacer layer consisting of 5- μm -thick posts or walls, fabricated in SU-8 2005 photoresist (MicroChem, Newton, MA) was overlaid on top of the micromagnet array to increase the thickness of the fluid film.

Basic Principles of Particle Assembly and Transport

The force on each nonmagnetic particle in a magnetic field gradient is proportional to the product of the net fluid magnetization $\langle \vec{M} \rangle$, with the fluid volume V displaced by the nonmagnetic particle (14, 15).

$$\vec{F} = \mu_0 V (\vec{M}_0 - \langle \vec{M} \rangle) \cdot \nabla \vec{H} \quad [1]$$

Substantial force on suspended nonmagnetic components ($\vec{M}_0 \approx 0$) is therefore a result of the nonzero fluid magnetization. This force is oriented oppositely to the force exerted on the magnetic nanoparticles in the same fluid. To minimize their potential energy, the nonmagnetic particles in the fluid assemble in the regions of local magnetic field minima, while the magnetic particles assemble in the regions of magnetic field maxima. In some cases, such as when no external magnetic field is applied, the magnetic field minima regions are located far away from the surface, as shown in Fig. 1*a*, and the nonmagnetic objects are forced to levitate well above the surface. However, when external uniform magnetic field is applied to the fluid, the regions of magnetic field minima are shifted down toward the surface, specifically to positions on the substrate where the trap's magnetic field subtracts from the external magnetic field. By using this phenomenon, colloidal particles and molecules can be concentrated on the surface and then redispersed by turning the external magnetic field ON and OFF (see Movie 1, which is published as supporting information on the PNAS web site). By reorienting the external field relative to the trap magnetization, the local regions of magnetic field minima can be shifted across the substrate (see Movie 2, which is published as supporting information on the PNAS web site). The quasi-static transport

Fig. 2. Assembly as a function of particle to trap size ratio. The assembly of micrometer- and submicrometer-sized beads onto magnetic traps of various shapes is demonstrated. The bead sizes in each of the images are as follows: $3\ \mu\text{m}$ (a), $2\ \mu\text{m}$ (b and g), $90\ \text{nm}$ (c), $5\ \mu\text{m}$ (d–f), $1\ \mu\text{m}$ (h), and $500\ \text{nm}$ (i and j). The beads assemble onto $5\text{-}\mu\text{m}$ circular magnetic traps in a, b, d, f, h, and j, whereas images c, e, and i show the assembly of beads onto rectangular magnetic traps with $3 \times 12\text{-}\mu\text{m}$ planar dimensions. Image g shows beads assembling onto the inverse magnetic pattern (i.e., $5\text{-}\mu\text{m}$ circular holes in a sheet of magnetic material). Images b, c, and g–j were taken after the fluid had evaporated, and images a and d–f were taken while still inside the fluid. It is curious that with submicrometer-sized beads sometimes hexagonal packing and other times fcc packing was observed. (Scale bars: $5\ \mu\text{m}$.)

model, illustrated in Fig. 1c, demonstrates that continuously shifting the minima regions in an externally rotating field can be used to transport the nonmagnetic particles linearly across the surface from one trap to the next.

Particle Assembly

Initial experiments, depicted in Fig. 1b, demonstrate that large single-layer arrays of micrometer-sized beads can be assembled onto magnetic traps inside a weakly concentrated solution of magnetic nanoparticles ($<0.05\%$ by volume) by static magnetic field. However, in more densely concentrated ferrofluids, a second layer of particles assembling hexagonally on top of the first layer was frequently observed. It was discovered that this aggregation problem could be solved by employing rotating uniform magnetic field to create dynamic steady-state particle patterns, as shown in Fig. 2. The patterns in Fig. 2 were produced on substrates patterned with magnetic traps of different shapes and sizes. In-plane rotating magnetic field was used to promote the formation of a single stable energy minimum for each particle, located directly on top of the magnetic trap. A stable energy minimum occurred only when the applied magnetic field was sufficiently strong to cause rotation of the trap's magnetization. This arrangement resulted in the magnetic field minima

being located directly on top of the magnetic trap at all times, which led to reliable packing of nonmagnetic beads on top of the traps, as shown in Fig. 1b. At the same time, particles that approached other areas of the surface were swept away by the magnetic nanoparticles circulating around the traps. Because the coercivity of the magnetized traps was found to be in the range of 50 to 70 G, it was possible to induce reliable assembly only in the presence of rotating magnetic field of $>100\ \text{G}$ in magnitude.

To determine an optimal set of assembly conditions, the rotation frequency and magnetic nanoparticle concentrations were varied by combination. It is desirable to use the strongest possible magnetic fields to obtain the largest average fluid magnetization and resulting force on the latex beads. However, fields of $>100\ \text{G}$ caused the formation of chain-like magnetic nanoparticle aggregates that frequently disrupted the assembly of beads. For this reason, $100\ \text{G}$ appeared to be optimal. The rotation frequency was varied between 1 and 40 Hz and completely error-free single-layer assembly of $5\text{-}\mu\text{m}$ latex beads on $5\text{-}\mu\text{m}$ circular magnetic traps was observed when the frequency was $>20\ \text{Hz}$.

For the same operating parameters ($100\ \text{G}$ external field, 20 Hz frequency, $0.1\text{--}0.2\%$ concentration of nanoparticles by volume), submicrometer beads could be packed on top of the traps into highly regular structures as illustrated in Fig. 2 h–j. When allowed to dry, the first layer of submicrometer colloidal particles acted as a template for the assembly of additional particle layers. Curiously, drying resulted in hexagonal packing in some regions on the substrate and in cubic packing in other places. Further investigations are needed to understand the nature of this phenomenon.

A combination of related phenomena is probably responsible for disrupting the formation of a secondary layer of beads in this experimental configuration. When external field is applied parallel to the substrate, it is energetically unfavorable for beads to chain up along the direction normal to the substrate, and beads are prevented from piling directly on top of one another. At the same time, movement of ferrofluid around the magnetic traps created localized fluid flow that swept away the beads that were not directly on top of the trap, thereby preventing the beads from chaining up parallel to the substrate. The richness of attractive and repulsive interactions nearby the substrate allows for a variety of colloidal patterns (both close-packed and separated) to be produced with very few defects. This technique also provides significant flexibility compared with other self-assembly methodologies based on particle sedimentation (19), electrostatic trapping (20), or morphological templating (21), which rely on purely attractive interactions to mitigate assembly of the intended components.

Particle Transport

Whereas in-plane magnetic field rotation results in a static region of magnetic field minima located directly on top of the magnetic traps, out-of-plane magnetic field rotation shifts the magnetic field minima regions continuously across the substrate. Conceptually, this shift can be described by the quasi-static transport model shown in Fig. 1. As can be seen, linear motion is induced only when the axis of magnetic field rotation is oriented perpendicularly to both the substrate normal and to the trap's magnetization. In contrast to the conditions required for particle assembly, the ability to transport materials across surfaces requires maintaining the trap magnetization in a constant direction. Thus, for this system the magnitude of the rotating field must be kept sufficiently low ($<60\ \text{G}$ in our case) to avoid switching of the cobalt traps. To achieve smooth motion over long stretches, the traps must be arranged sufficiently close to one another to form a periodic structure of potential energy for any given direction of the external field. In this arrangement, a traveling potential wave moving along the line of the trap's

between nonmagnetic particles are significantly weaker in more dilute magnetic nanoparticle concentrations.

The bead velocity as a function of frequency was estimated to determine whether experimental results agreed with theoretical predictions. In simulations, it was assumed that the traps were uniformly magnetized, that their magnetization did not vary with the applied field, and that the remanent flux density in the traps was 0.25 tesla, which is consistent with measurements by alternating gradient magnetometer. It was assumed that magnetic particle concentration was constant (equal to the bulk value everywhere). By using these assumptions and fluid viscosity values supplied by the vendor of the magnetic fluid, it was found that the maximum velocity of a 3- μm bead above a rectangular array of 5- μm -diameter circular traps spaced 3 μm apart is expected to be 34, 19, and 8 $\mu\text{m/s}$ in the highest, medium, and lowest nanoparticle concentrations, respectively. These values agree closely with the data for lower magnetic nanoparticle concentrations, and they agree with data for the highest nanoparticle concentration in the linear regime between 0 and 8 Hz. However, the model neglected the magnetic interactions between nonmagnetic particles and could not predict bead aggregation. Therefore, the model cannot explain the experimentally observed increase in bead aggregate velocity of >8 Hz.

Particle Sorting

It also was noticed that particle motion is strongly affected by the form of the trap pattern on the surface. The movement of particles across a discontinuity in two magnetization patterns (i.e., grain boundary of two different magnetic trap arrays) resulted in interesting transport phenomena, as shown in Fig. 5. As can be seen in Movie 4, which is published as supporting information on the PNAS web site, particle movement is stunted in some regions of the substrate, whereas particles can easily pass through other regions on the substrate. The reason for this phenomenon is that the traveling potential is disrupted at the boundary between two different magnetic patterns. The disruption may provide a potential energy barrier that is sufficiently large to prevent particles from continuing along the magnetic track. The disruption can be caused by a physical grain boundary, as shown in Fig. 5, for example, where the contrast region is due to the boundary between a pattern of circular magnetic traps and a pattern of rectangular magnetic traps. However, the traveling potential can also be disrupted locally within a uniform array of magnetic traps by reversing the magnetization of a few individual traps in the array. Point and line defects may provide sufficient potential energy boundaries such that particles are focused away from these magnetization discontinuities and channeled toward particular tracks under the influence of a global rotating bias field. Thus, ensembles of particles can potentially be controlled with local precision by carefully controlling the local magnetization patterns in a uniform array of magnetic traps. It is envisioned that arrays of perpendicular magnets (i.e., magnets whose easy axis is aligned perpendicular to the substrate) will be

particularly helpful for this application, because they allow for one of the trap's poles to be embedded deep inside the surface. However, perpendicular magnets are not necessary to achieve this effect.

Conclusion

The main purpose of this work was to develop methods for magnetically manipulating materials in a programmable fashion without requiring their attachment to magnetic particle carriers, which is the most common magnetic manipulation scheme (22, 23). Many potential applications are envisioned for the techniques developed in this work. For example, the ability to bring nonmagnetic components toward a surface by cycling the magnetic field ON and OFF (Movie 1) may be used to assist biological sensing applications. Traditionally, sensor efficiency is limited by the relatively slow diffusion of target molecules to sensor regions of a substrate. The magnetic manipulation techniques provided here can drastically speed up hybridization times by promoting the target molecules to sample regions of a surface more quickly. The particle assembly techniques also may assist the fabrication of various emerging devices that require integrating micro- and nano-sized components into useful systems. Some applications in medical devices may require the precise arrangement of biological materials (24), such as cells, viruses, and bacteria, and photonic and electronic applications may require the ability to position colloidal particle arrays (5) or electronic components, such as nanowire transistors (25) and display elements (6).

The proposed method may have certain limitations, and a number of open questions remain. A fundamental limitation is that magnetic forces are generally weaker than forces due to electric fields and may not be optimal for manipulating colloidal objects whose largest dimension is below ≈ 50 nm. One important issue not addressed by this work is the method for fixing the materials onto the substrate once they are assembled. Indeed, the developed manipulation techniques are not a stand-alone process, and they must be assisted by surface forces, based on molecular recognition, morphological templating, and/or photo-initiated chemical reactions, which can freeze the intended patterns in place once they have been assembled. Another open question is the ability to remove the ferrofluid after the assembly process and the possible effects of ferrofluid on living cells and viruses. Biologically compatible ferrofluid has not been used in the reported experiments. As mentioned in the introduction, magnetic recording techniques will be needed for independent control over particle trajectories and assembling patterns with local precision. Conventional recording methodology may require some rethinking for such applications. Open questions concerning the proposed magnetic manipulation and assembly methods remain to be addressed.

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