Magnetoacoustic Assembly of Colloidal Alloys

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Self-assembly of microstructures has become a widely used assembly technique due to its high efficiency and low cost. This methodology depends on the spontaneous formation of lattices, and does not require special instruments. Different approaches have been developed in order to induce the self-assembly interaction of particles. Among them magnetic field induced assembly has advantage in controllability and versatility. Previously we applied a uniform field to magnetic and non-magnetic microspheres dispersed in ferrofluid solution, and changed the ferrofluid concentration as a parameter to realize the assembly of different structures including square, honeycome and kagome lattices. In this work we enhance this approach by adding acoustic field to the system. By combining both magnetic and acoustic fields, large lattices were achieved and new structures such as quasi- 3D, and closed packed super-structured rings were observed. In addition, when we used epoxy to achieve solid boundary, standing waves were generated to assemble particles into regular patterns on the macro-scale while preserving the micro-structures. We also used a pair of piezoelectric transducers and

modified their phase difference and frequency to change the assembly position of particles. To our knowledge, this is the first example of multi-scale self-assembly technique by using a combination of acoustic and magnetic fields.

Introduction

Matematerials are engineered artificial materials created to obtain unique microscopic properties. One of the most important characteristics of these fabricated materials is their structure or spatial organization, which determines their behavior and control over propagation of light, sound and heat. Much research has been performed in order to fabricate these artificial crystals, including lithography, and robotic assembly. However, these techniques can be expensive and sometimes unreliable. Self-assembly, a "bottom-up" technique, has drawn a lot of attention due to its simplicity and free energy minimization. Previous work has used magnetic fields to guide the arrangement of magnetic and nonmagnetic polystyrene beads into the formation of chains and tile structures, including square, honeycomb, and kagome lattices. One of the main advantages of this method is the fact that interaction strength in particles can be precisely controlled by changing the strength of the magnetic field, which can be done with a relatively simple procedure. This procedure is based on the magnetic dipole to dipole interaction, in which particles are treated as point dipoles under the presence of an external magnetic field and their interaction can be described with the equation

$$U_{12} = \mu_0(m_1 m_2)/4\pi|r_{12}|^3$$

where U represents the energy of the pairwise interactions between the particles, m 1 and m2 are dipole moments and r is the distance between the two point dipoles [1]. Ferrofluid is used in the

experimental section in order to create a diamagnetic permeability in the solution without the necessity of obtaining a diamagnetic material, which can be difficult to find. As a result of including ferrofluid as the magnetic medium, dipole interactions can easily be controlled by changing the ferrofluid concentration in the solution. It has been found that larger single domain crystalline structures are formed when the net dipole density is close to zero, and that in order to minimize the net dipole density, the ratio of the dipole magnitudes between magnetic and nonmagnetic particles has to be inversely proportional to their relative concentrations in the crystal. The moment in paramagnetic and diamagnetic particles can be described independently with the equation

$$\vec{m}\text{m,n} = 3\left(\frac{\mu_{m,n} - \mu_f}{\mu_{m,n} + 2\mu_f}\right)V\vec{H} = \overline{X}(m,n)V\vec{H}$$

Where μ_m, μ_n and μ_f represent the magnetic permeability of paramagnetic, paramagnetic, and ferrofluid respectively [1]. In the equation above it can be seen that, if the magnetization of magnetic or non-magnetic particle is greater than the magnetization of the ferrofluid μ_f, the equation becomes positive, meaning that the moment of the bead will align parallel to the external magnetic field. If the opposite occurs, where the magnetization of the bead is less than the ferrofluid as in the case of non-magnetic particles, the equation will become negative and the moment of the colloid will align anti-parallel to the magnetic field. In other words, ferrofluid is used as a control parameter to give the particles their magnetization characteristics and program different structures.

A more promising way of fabricating the metamaterial is by combining magnetic and acoustic fields, where the vibrations created by a piezoelectric material with a relative small voltage will guide the colloids in the ferrofluid suspension towards a larger formation of

clusters. Previous work has shown that it is possible to program the assembly of polystyrene beads to nodal positions created by varying the phase difference between the counter-propagating waves [2]. The potential energy on particles due to acoustic field is described by the following equation:

$$U = \frac{V}{4\rho c^2} \left[2f_1 \langle p_1^2 \rangle - \frac{3f_2}{k^2} \left\langle |\nabla p_1|^2 \right\rangle \right]$$

Where V is the velocity of the particle, c is the velocity of sound in the fluid, p is the pressure, and k is the bulk modulus of the particles. One important aspect from this equation is how the potential energy of the alloys depends on the gradient of pressure. In this case, the particles will be assembled to the pressure nodes created by the acoustic fields to minimize free energy.

Another advantage of using an acoustic field in addition to a magnetic field is that particles will be pushed away from the substrate in the z direction, which can enable the arrangement of lattices as 3-D superstructures. This is due to the fact that pressure nodes are created by the acoustic field and the potential energy of the particles are affected by the dynamics of the fluid due to this field.

Methods and procedures.
Materials: Magnetized polystyrene beads (MyOne Dynal beads, Invitrogen) with a diameter of 2.7 um and Nonmagnetic polystyrene beads (Fluoro Max, Polymer microspheres, ThermoScientific) with a diameter of 4.8 um were used when preparing the heterogeneous solution with a concentration of about 1% solids. The ferrofluid aquous suspension (EMG 807 Series Ferrofluid, FerroTec) consisted of magnetic nanoparticles in the range of 12nm applied at 2% volume fraction of solids.

Substrate preparation: Glass slides and cover slips (VWR ,US) were made hydrophilic by cleaning them with acetone and placing them in a Plasma Asher (Emitech K-1050X CINEMAS) for 30 seconds at 30Watts. This was done to avoid the particles from adhering to the surface of the substrate when the ferrofluid concentration was increased. Furthermore, slides were coated with PEG (Polyethylene glycol) by submerging them in a 10mg/100ml solution for about 24 hours to increase hydrophilic behavior. Glass slides and cover slips were then rinsed with iodized water and dried with N2 previous to use. Another alternative to our substrate was the use of a larger glass slide covered in 10um thickness SU-8 photoresist, where glass "wells" of $1cm^2$ were then created by removing the photoresist. The advantage of using this technique is to increase the number of beads relative to the space on the substrate. In other words, the volume of solids is increased and therefore the beads come into closer contact.

Sample preparation: In order to form the crystals, a heterogeneous solution consisting of magnetic and nonmagnetic beads was prepared by combining 470ul of nonmagnetic beads and 30ul of magnetic ones in a small tube. The sample was then vortexed to assure dispersity of the mixture. A constant ratio between the particles was maintained; however, the ferrofluid concentration was mixed in different volumetric ratios to determine the different structures when changing this parameter. For instance, for a 9ul bead solution and 1ul ferrofluid suspension, the volume fraction of the ferrofluid was considered to be 0.1% and when the ferrofluid concentration was 25% (by combining 7.5ul of beads and 2.5ul of ferrofluid) the volume fraction was increased to 0.5%. This is one of the main advantages of our methodology since the volume fraction of ferrofluid is considerably reduced when compared to previous work. After the final colloidal suspension consisting of the ferrofluid and beads was mixed, it was vortexed one

more time to ensure equal distribution of the ferrofluid in the liquid. The solution was then placed between the substrate and cover slip (3.75ul - 4ul) and non-drying immersion oil was distributed around the edges to reduce fluid convection and microsphere buildup. Mineral oil also proved to increase the durability of the experiment for several hours. This procedure was taken for several ferrofluid concentrations, including 10, 15, 20, 25, 30 and 35 percent. Also, higher volume solid fraction was obtained by centrifuging the magnetic and nonmagnetic beads (3,000 rpm for 3 minutes) before mixing them with the ferrofluid and by removing the excessive effluent. For instance, in order to obtain three times the concentration of beads, about 333ul of effluent was removed from a 500ul bead suspension.

Magnetic field: In order to create a magnetic field, current from a power supply is passed through air-core solenoids fitted with iron cores (Fisher Scientific, Pittsburgh, USA) The magnetic field is controlled with Labview, where magnitudes of 10, 20, 40, and 60 gausses in the z-direction were used to perform experiments. A 90% current duty cycle was utilized when only a magnetic force was applied to the solution to give relaxation to the system and it was increased to 95-98% when acoustic field was added to avoid dispersion of the beads due to this field.

Applying acoustic field: Behavior of particle colloids under the force produced by an acoustic field was observed by using a customized piezoelectric transducer (APZ International, 0.5cmX3.5cm) placed on the back of the substrate. A sinusoidal voltage was applied to the material by using a wave generator with a frequency of 2.93Mhz to match the resonant frequency of the piezoelectric material. The voltage applied in our experiment varied from 2V, 5V and 10V in intervals of about one hour each with the purpose of bringing the particles closer together and achieving larger configurations.

Microscopy: Microscopy was performed with a DM LM fluorescent microscope (LEICA, Bannockburl, IL, USA). 40X magnification was used to obtain pictures of different structures using a CCT camara connected to the microscope. Fluorescent images were obtained using red filter cubes that permit us to easily visualize non-magnetic beads and their configuration. A magnification of 10X was also used to observe the behavior of the particles due to the acoustic field.

Results and Discussion

Different crystal structures were observed by changing parameters such as ferrofluid concentration, magnetic and acoustic field. In the case where the acoustic field applied was weak compared to the forces driving the particles together, we were able to observe ring structures also seen in a system with no acoustic field. Figure 1 shows some of the most representative ring configurations obtained by changing the ferrofluid concentration and by maintaining an acoustic amplitude of 2V. As it can be observed in the figure, the various ring phases observed in experiments include R1, R2, R3, R4, R5, R6, and some of their inverse ring configuration. When the ferrofluid concentration is low, such as in the case of 0.1%-0.6%, structures composed of one magnetic particle and multiple non-magnetic particles can be formed. The inversed case, in which there is one non-magnetic particle and multiple non-magnetic particles, is mostly seen in occasions where the ferrofluid concentration increases.

Chain conformations and tile structures were also observed in the case where the acoustic field was relatively weak. Figure 2 shows some of the chain phase structures obtained for different ferrofluid concentrations, including one magnetic particle versus two non-magnetic beads, one magnetic and one non-magnetic bead, and two magnetic versus one non-magnetic particle. The formation of these

chains is highly dependent on the ratio of paramagnetic and diamagnetic colloids and also on the ferrofluid concentration. Larger structures such as square and honeycomb lattices can also be created under the specific conditions where the acoustic force is maintained low. Square lattices, for instance, have been observed for 0.5% ferrofluid concentration and a ratio of 1:1 between magnetic and nonmagnetic beads. Honeycomb lattices, however, have been difficult to find in larger arrays due to the lack of concentrated number of particles required for interaction. Furthermore, the formation of this type of structure needs a relatively high level of ferrofluid concentration in order to achieve a zero dipole moment per unit cell for optimal interaction.

Figure 1: RIng formations after application of small acoustic field. In the case of low levels of ferrofluid, R1, R2, R3, R4 and R5 ring types are created. When the levels of ferrofluid concentration is higher, their inverse are obtained as well as R6* and R7*,where * denotes inverse configuration.
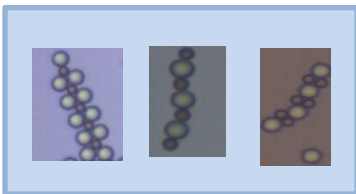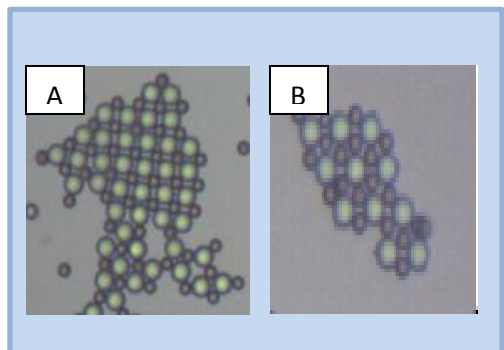

Figure 3: Chain structures with low acoustic field

Figure 2: Tile structures forming: A) square lattices and B) Honeycomb structures

Transition to acoustic field

As previously mentioned, acoustic field forces are introduced in the system to increase the interaction between particles and induce larger lattice configurations. When increasing the acoustic field from 2V to 5V or 10V, it was possible to create super- structures not present in lower amplitudes of acoustic field. As it can be observed in Figure 4, quasi 3D structures are formed, where non-magnetic beads are suspended in two different layers due to the influence of the acoustic force pushing the fparticles against gravity, allowing the beads to arrange into lattices to achieve energy minimization. As an example, by increasing the amplitude voltage in the order 5V and 10V in a 0.5% ferrofluid sample, ring structures with 6 or 8 non-magnetic beads surrounding one magnetic particle are formed. Such structures are not seen in the case where the acoustic force is zero or too low because of their size difference and their geometry constrictions in two dimensions. More importantly, these rings have the ability to form lattice structure as seen in figure 5, which suggests the possibility to form a large variety of super structures by combining two different fields

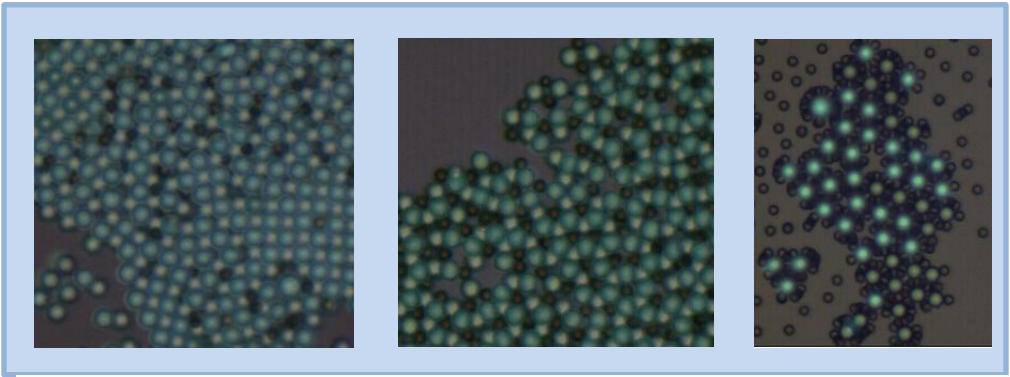Figure 4: Quasi- 3D structures created with high acoustic field

Figure 5: Tile structures generated with quasi-3D structures with high acoustic field

Controlled spatial distribution

In order to have a more controllable distribution of colloidal aggregates on the substrate, an acoustic field was generated by using a piezoelectric material attached to the back of a glass slide. In previous work, it has been demonstrated that acoustic fields can organize the location of particles depending on the amplitude, phase, frequency, and number of transducers used in the glass slide. In order to investigate the behavior of the acoustic waves in our experimental set-up, one piezoelectric material was placed on the center of the back of the substrate and immersion oil was placed around the glass slide. The results of this experiment are shown in figure 6A, where it is seen that the acoustic field creates horizontal nodes around the edges of the substrate. This demonstrates that the acoustic field can be used to bring the particles together at particular locations and promote assembly. However, it is very difficult to control the exact location of the nodes with submersion oil due to its non-viscous nature. As a consequence, the infiltration of the oil into the sample changes the boundary conditions around the edge of the cover slip, resulting in an irregular nodal pattern.

A more promising way to control the acoustic field is by using epoxy around the edges. When the epoxy hardens, it reflects the acoustic waves at all four sides of the glass, creating square patterns as seen in figure 6B. In other words, since the epoxy creates four solid walls around the solution, the boundary conditions become more regular and as a result the patterns created by the acoustic field also become more regular.
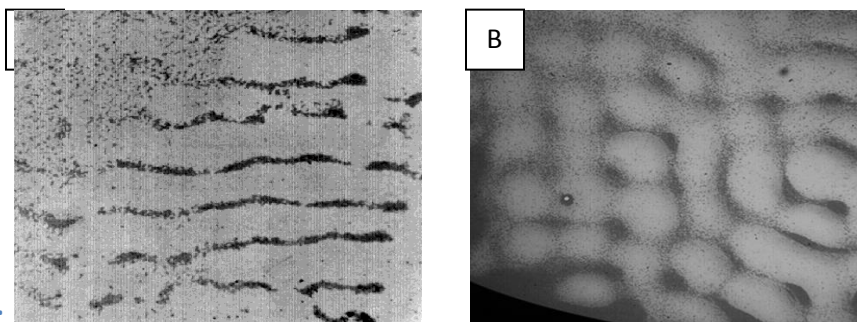

Figure 6: **Nodes formed around edges due to acoustic field using: A) emersion oil and B) epoxy.**

The effects of phase difference and frequency were investigated by placing two piezoelectric transducers on the back of the substrate perpendicular to each other. Video taken from these experiments demonstrate that changing the phase in one of the transducers moves the particle formation to a different location. For instance, Figure 7 shows the effects of phase difference by changing one of the transducers to 0°, 90° and 180° phase, where an evident change in the groping site is seen. Similarly, in the case of frequency difference, This nodal formation indicates the possible programmable control of assembly in the micro-scale.
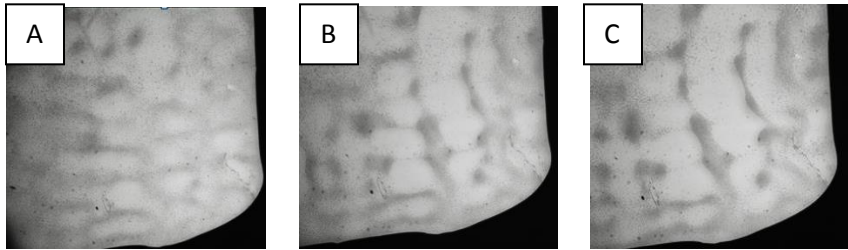
Figure 7: Effects of phase difference applied to two piezoelectric transducers on the back of the substrate. The introduction of acoustic field shows the possibility of micro scale control of particle formation. A) shows a phase difference of 0°, where each transducer has 0° phase. B) Phase in one of the transducers is changed to 90°. C) Phase difference changed to 180°.

Conclusion

It was shown that by combining magnetic and acoustic fields to our system, nodes made by the acoustic field could be controlled to generate a regular macro-scale pattern on the substrate. Also, due to a phase difference induced by attaching an additional piezoelectric actuator, the location of particle assembly was shown to change. In addition to macro-scale assembly, it was demonstrated that new quasi-3D superstructures were observed due to the mechanical interaction of the acoustic field on the particle. A larger lattice on the substrate indicates the possible application of these materials in photonic crystals when particles are reduced to the nano-scale.

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