Iron nanoparticle assemblies: structures and magnetic behavior

D Farrell$^{1,2}$, Y Cheng$^1$, S Kan$^1$, M Sachan$^1$, Y Ding$^1$, S A Majetich$^1$ and L Yang$^3$

$^1$Physics Department, Carnegie Mellon University, Pittsburgh, PA 15213, USA
$^2$London Centre for Nanotechnology, University College London, London, WC1E 7HN, UK
$^3$National Synchotron Light Source, Brookhaven National Laboratory, Upton, NY 11973, USA

Email: sm70@andrew.cmu.edu

Abstract. Self-assembly of spherical, surfactant-coated nanoparticles is discussed, and examples are presented to demonstrate the variety of structures that can be formed, and the conditions that lead to them. The effect of the concentration on the magnetic properties is then examined for 8.5 nm Fe nanoparticles. Dilute dispersions, arrays formed by evaporation of the dispersions, and nanoparticle crystals grown by slow diffusion of a poorly coordinating solvent were characterized by zero field-cooled magnetization, remanent hysteresis loop, and magnetic relaxation measurements. The average spacing between the particles was determined from a combination of transmission electron microscopy and small angle x-ray scattering. In the arrays the spacing was 2.5 nm between the edges of the particle cores, while in the nanoparticle crystals the particles were more tightly packed, with a separation of 1.1 nm. The reduced separation increased the magnetostatic interaction strength in the nanoparticle crystals, which showed distinctly different behavior in the rate of approach to saturation in the remanent hysteresis loops, and in the faster rate of time-dependent magnetic relaxation.

1. Introduction

Monodisperse nanoparticles coated with organic surfactants have demonstrated the ability to self-assembly into well-ordered arrays [1, 2], and when the nanoparticles are magnetic, this process enables great control of the magnetostatic interactions. In some types of magnetic nanoparticle arrays, such as FePt arrays for possible magnetic recording media [3], it is undesirable for the particles to interact with each other. With strong interactions, the state of one multi-particle bit could affect the state of its neighbors, leading to a reduced signal-to-noise ratio.

Understanding how to control self-assembly and take advantage of strong magnetic interactions could have significant consequences. With sufficiently large magnetic forces, the particles will form chains when an external magnetic field is applied, as in ferrofluids made from monodomain particles [4] and magnetorheological fluids made from much larger, multidomain particles [5,6]. The important requirements are that the collective behavior of a nanoparticle assembly is different from that of well-dispersed nanoparticles, and it can be reversibly controlled by an external stimulus.

Here we limit ourselves to monodomain particles, and focus on interactions of particles within arrays, rather than chains. There have been extensive studies of dilute dispersions of magnetic
nanoparticles [7-14], but far fewer of interactions in arrays where the concentrations are much higher [15-17]. We examine how subtle differences in the particles and self-assembly conditions lead to different kinds of structures, and describe the strengths and limitations of different approaches. The magnetic properties of the ordered assemblies are presented, and the range of magnetic interaction strength that is possible with these self-assembly methods is discussed.

Iron is used as the nanoparticle material, even though this restricts our study to air-free conditions, because it has a large moment and therefore leads to maximum magnetostatic interaction strength for a given particle size. These particles are synthesized by high temperature solution chemistry methods, and they are coated with a layer of surfactant molecules [18]. An individual particle may have hundreds to hundreds of thousands of atoms, and the atomic magnetic moments are exchange coupled into a single magnetic domain with a giant moment, so that the particle itself acts like a giant spin. Unlike in atomic crystals, where the moment per atom and the separation between moments are fixed quantities, in the nanoparticle arrays both the magnitude of the moment and the inter-moment spacing can be varied.

It is intriguing to consider the analogy to the formation of magnetic domains in atomic crystals, through the balance of exchange and magnetostatic interactions. Here we will examine the effects of changing the particle separation and the degree of structural ordering on the magnetic properties of Fe nanoparticle arrays (figure 1).

![Figure 1. Schematic showing the types of nanoparticle samples compared in this study: dilute dispersions, arrays self-assembled by evaporation of the dispersions, and nanoparticle crystals formed by slow diffusion of a poorly coordinating solvent into the dispersions.](image)

2. Self-assembly of nanoparticles into arrays
These nanoparticles were synthesized by heterogeneous nucleation methods that have been reported previously [18]. The particles used for magnetic and neutron scattering measurements were handled in air-free environments at all times. Those used for transmission electron microscopy (TEM) and x-ray scattering measurements were exposed to air, but these measurements were used solely for structural information about the arrays, which would not be affected. The iron oxide shell thickness for the minimally oxidized particles was roughly 0.5 nm, and independent of the particle diameter, based on a combination of TEM, x-ray fluorescence, and specific magnetization data with a core-shell model [18].

Self-assembly of nanoparticle arrays is a deceptively complex phenomenon. It always requires monodisperse, surfactant coated particles in a liquid. For small (< 20 nm), sterically stabilized nanoparticles, the solvent must be organic (figure 2). The magnetic forces are much weaker than the van der Waals and other non-magnetic forces; otherwise chains would form rather than arrays. Once
Figure 2. (a) 10 nm Co nanoparticles evaporated from a hexane solution form a well-ordered array. Note that the self-assembly process has the potential for defect tolerance, as seen in the well-ordered regions surrounding the site vacancy in the lower central region. Also note that a few smaller particles have been expelled to the edges of the array, much as impurities may segregate to the grain boundaries within a bulk solid. (b) 10 nm Fe₃O₄ nanoparticles evaporated from an aqueous solution form a gel-like structure with chains of particles. Here the surfactant coating is tetramethylammonium 11-aminoundecanoate, which leads to an interparticle spacing of ~1 nm, compared with the 2.5 nm between the edges of particles in (a).

nucleation occurs, the arrays grow in size until they impinge on one another, very much like the grains of an atomic crystal.

The most common technique for forming the self-assembled nanoparticle arrays uses solvent evaporation to increase the particle concentration and drive the ordering transition, predicted for hard spheres with a volume concentration above 0.46 [19, 20]. The particles are synthesized in a high boiling point solvent, which would evaporate very slowly at room temperature. To speed up the process, the particles are temporarily flocculated by the addition of a poor coordinating solvent (ethanol), and collected at the bottom of the reaction flask with a magnet while the excess liquids are decanted. A low boiling point, good coordinating solvent (hexane or toluene) is then added to redisperse the particles. To form nanoparticle arrays by the evaporative method, a drop of the hexane or toluene dispersion is evaporated on a substrate, and capillary forces and disjoining pressures cause the particles to pack together. The typical drying time in this case is less than five minutes. Typical particle concentrations for 4-9 nm Fe particles are on the order of 10¹⁴-10¹⁵ particles/cm³ for hexagonal arrays similar to that shown in figure 2 (a). With more concentrated dispersions, there is significant aggregation in the bulk region or the solution, and TEM images show some arrays with fcc lattices oriented along (100) axes. When nucleation of the array occurs at a substrate, the bottom layer is always hexagonal, though the stacking may be hcp, fcc, or a mixture [21].

While there have been many published TEM images of beautifully ordered arrays, it remains difficult to generate macroscopic area, perfectly ordered regions in a reliable process. This limitation may limit the use of the FePt nanoparticle arrays for data storage, unless it can be circumvented. One solution is to use templates to control the ordering length scale and the orientation of the array (figure 3). Here the corners are low energy sites for nucleation of the array, and if the number and location of nucleation events can be controlled, then it is feasible to make macroscopic arrays in a repeatable fashion.
Figure 3. (a) and (b) TEM images at low and high magnification, respectively, showing template effects on nucleation and array orientation.

In multilayer arrays, the maximum length scale for structural ordering is also limited by cracking (figure 4). The surfactant that holds the particles together has a wax-like consistency at room temperature and offers little mechanical stability.

Figure 4. TEM image of evaporated multilayer array of Fe nanoparticles showing the disruption of large scale ordered regions by cracks.
An alternative self-assembly technique uses colloidal crystallization to grow nanoparticle crystals [22]. The advantage of this approach is that the self-assembly is completed prior to drying. Once the drying front passes through in evaporative array formation, the particles are fixed in place. Since that process is rapid, many structural defects can be quenched in. In the colloidal method, a few mL of the toluene dispersion is placed at the bottom of a test tube. Without evaporation or contamination, this dispersion would be stable for years. In order to drive self-assembly, a poor coordinating solvent is slowly diffused into the mixture. This is accomplished by gently covering the toluene solution with a few mL of an immiscible liquid, such as 2-propanol or ethanol, or both. Over a period of two to four weeks, there is slow diffusion of the poor solvent downward into the particle-rich region, which gradually destabilizes the dispersion. Because the process is slow, the particles can come closer to finding their minimum energy positions in a close-packed lattice. Here the limitation in the size of the ordered region is determined by the size that the agglomerate reaches prior to sedimentation. The walls of the test tube show evidence of nucleation, presumably at defects, which suggests that templating could be used to control the size and orientation of the nanoparticle array. Scanning electron microscopy (SEM) shows that the particles are three-dimensional, and they range in size from one to ten microns. It is difficult to obtain useful information from TEM images because the thickness limits the electron transparency. Near the edges of the nanoparticle crystals we have observed evidence of multiple grain orientations, and also of some residual disordered regions, but it is unclear whether this is representative.

3. Magnetic behavior of the assemblies

For Fe particles in the size range studied here, the dipolar field at the center of one particle due to its neighbor is on the order of hundreds of Oersted. Because the particles are close together, higher multipole interactions may also be important. Between atomic moments, the exchange strength decays roughly exponentially with increasing distance, and for edge-to-edge spacings of > 1 nm between the Fe cores in the samples studied here, exchange interactions are assumed to be negligible.

Not all magnetic nanoparticle arrays have significant magnetostatic interactions. We compared the magnetic response of the same sample oriented parallel and perpendicular to the applied field to determine the threshold for significant DC interaction effects. Here stacks of TEM grids containing nanoparticle arrays were embedded in silicone grease for rapid transfer from the glove box to the SQUID magnetometer. If the particles have minimal interactions, measurements parallel and perpendicular to the plane of the grids will yield identical results. This turns out to be the case for Fe particles smaller than 6 nm, with a 2.5 nm edge-to-edge spacing, and is certainly true for 4 nm FePt nanoparticles in arrays that have been proposed for data storage media [3]. If the particles have stronger interactions, then the multilayer array acts like a magnetic thin film in terms of shape anisotropy, and favors in-plane magnetization. This leads to a slower approach to saturation when the applied field is perpendicular to the plane, relative to that for the hysteresis loop with a parallel field.

Figure 5 shows a comparison of the zero field-cooled magnetization as a function of temperature for 8.5 nm Fe particles in dilute dispersion (0.01 vol. %), in arrays formed by evaporative self-assembly, and in nanoparticle crystals made by colloidal self-assembly. Of the three samples, the dilute dispersion is expected to most closely approximate the behavior of non-interacting particles. With 6.7 nm particles, 5-10 K downward shifts in the blocking temperature, or temperature of the maximum magnetization, were observed between the dilute solution and the arrays [23]. Above this temperature the magnetization dropped steadily. With the larger particles, the blocking temperature shifts upward, as expected, but the curve also broadens significantly, even for the dilute dispersion. In the nanoparticle crystals, the blocking temperature appears to shift upward again and be comparable to that in the dilute case. The most significant feature of the zero field-cooled magnetization shown in Figure 5 is that all three curves show broad, flat magnetization curves.

Figure 6 shows the remanent hysteresis loops for the same samples. It is surprising that the coercivities of the three samples do not vary significantly. The most striking different is in the rate of
Figure 5. Zero field-cooled magnetization versus temperature, for 8.5 nm Fe nanoparticles in dilute hexane dispersion, in arrays evaporated from this dispersion, and in nanoparticle crystals grown by the colloidal method. The upward turn above 140 K is associated with melting of the solvent.

The approach to saturation, which is particularly slow in the colloidal crystals. The magnetic relaxation as a function of the natural logarithm of time is shown in Figure 7. Note that none of the samples has a constant magnetic viscosity over the time window from one minute to ten hours. Earlier work on dilute dispersions of 5.5 and 8.0 nm Fe particles using a time window of $10^5$-10$^4$ s showed that apparent magnetic viscosity can vary significantly over time [24,25]. The changes in the slope can be viewed in terms of differences in the distribution of energy barriers to relaxation. In the time window studied here, the arrays have a slower relaxation rate than the dilute sample at times above $t/t_0=5$, or about 7.5 minutes. This characteristic “kink” in the relaxation rate has also been observed for smaller Fe nanoparticle arrays [26]. The nanoparticle crystals have no kink in the relaxation, and in fact demagnetize faster than the other samples.

There were two main differences between the particles in the arrays made by evaporative self-assembly, and those in the nanoparticle crystals formed by colloidal self-assembly, the separation between particles and the length scale of the structural order. The size of the average particle separation was determined from TEM images for the arrays, but the colloidal crystals are too thick to be electron transparent. From a combination of TEM to determine the size of the original particles and small angle x-ray scattering (SAXS) to determine the average center-to-center spacing, the thickness of the barrier between particles can be determined [27,28]. Since the nanoparticle crystals can be redissolved in toluene, it is possible to verify by TEM that the colloidal crystallization process does not change the particle size during the course of a few months. [29]. For the samples in Figure 6, particles in the arrays have an edge-to-edge spacing of 2.5 nm while those in the colloidal crystals are separated by only 1.1 nm.

The nanoparticles in the colloidal crystals therefore have much stronger magnetostatic interactions. The length scale of ordering can vary considerably, depending of the rate of formation of the arrays. Figure 8 shows SAXS data collected on a two-dimensional detector and circularly averaged. In earlier studies [27, 28] we reported that shorter colloidal crystallization times yielded diffraction rings, while longer times gave sharper spots. This is much like the difference in electron diffraction patterns between small, randomly oriented crystals and a few large crystals. Figure 8 shows the difference between a well-ordered nanoparticles crystal with a face-centered cubic structure with a...
Figure 6. (a) Remanent hysteresis loops of 8.5 nm Fe nanoparticles in different samples, at 10 K. The nanoparticle crystals have a slower rate of approach to saturation, that begins just above the coercivity. (b) The same loops over a smaller range of the applied field show that the arrays also have a slower rate of approach to saturation than the dilute sample, though the degree of deviation is much smaller.

lattice parameter $a = 16.7$ nm, and a poorly ordered assembly made by rapid evaporation. The disordered assembly shows a broad peak associated with local close packing, but no more. During the slower colloidal crystallization process, the particles are able to pack closer together, and the surrounding liquid enables the particles to diffuse around until they find lower energy positions. During rapid evaporation, the particles may be locked into non-equilibrium positions once the drying front passes through.
Figure 7. Magnetization as a function of time. Here the sample is saturated, and then the field is reduced to zero. The magnetization and time are normalized relative to the initial values after stabilizing at zero field.

Figure 8. SAXS patterns of nanoparticle crystals showing an FCC structure, and of rapidly quenched assemblies, both made from 8.5 nm Fe nanoparticles.
4. Discussion

It seems at first contradictory that the nanoparticle crystals simultaneously have the slowest rate of approach to saturation in the remanent hysteresis loops, yet also the fastest rate of magnetic relaxation. The former is normally associated with the presence of high energy barriers, and the latter with small ones. This paradox can be understood by examining the quantities determined by these measurements.

In a remanent hysteresis loop we learn about how the energy barrier distribution is modified by an applied field. For an ensemble of non-interacting uniaxial Stoner-Wohlfarth particles [30], the energy barrier $\Delta E$ is given by

$$\Delta E = KV \left[ 1 - \left( \frac{H}{H_K} \right)^2 \right],$$

where $K$ is the magnetocrystalline anisotropy, $V$ is the particle volume, and $H_K = 2K/M_s$ is the anisotropy field. The energy barrier $\Delta E$ approaches zero as $H$ approaches $H_K$, and the particles switch to align with the external field. Fe is not a uniaxial, but the anisotropy field can be estimated [31] to be on the order of 1.4 kOe, using the anisotropy estimated from the blocking temperature of the dilute dispersion and the saturation magnetization of the particles, which is less than the bulk value. This anisotropy field would have to be more than twenty times larger to explain the observed approach to saturation based on anisotropy alone, and at the same time, the local magnetostatic fields are going to be nowhere near this large.

In the nanoparticle assemblies, the slow approach to saturation in the remanent magnetization hysteresis loops is similar in some ways to the rotational effects in an ordinary hysteresis loop. In the ordinary loop for a bulk ferromagnetic crystal, the domain walls move at low fields, and then spins within the single remaining domain rotate to align parallel with the applied field at high values of $H$ [32]. Remanent hysteresis loops are normally considered to have no rotational contributions. In zero applied field for non-interacting monodomain particles, the moment will lie along one of the easy axes. The Fe nanoparticles have six equivalent (100) easy axes, and so in remanence there are size possible directions for the magnetization vector. When there are strong magnetostatic interactions, the local field may be nonzero, and it may stabilize easy axis directions that are not parallel to the applied field. However, the slow rate of approach to saturation at 10-20 kOe cannot be due to an extremely large local field, since this would exceed the Lorentz cavity field within an atomic crystal of pure Fe. The presence of multiple grains within the nanoparticle crystal contributes to magnetic disorder, which would also slow the rate of approach to saturation. This is consistent with the nearly logarithmic magnetic relaxation shown in figure 7, indicating a distribution of energy barriers.

If the magnetostatic effects are strong enough to generate a domain-like structure within the nanoparticle arrays, the magnetic relaxation from a fully saturated state would be expected to be rapid, since domain formation minimizes the total energy. In nanoparticle crystals containing multiple grains, there would be many low energy sites to nucleate reverse domains. In the evaporated self-assembled arrays, the fact that the relaxation is slower than in the dilute sample suggests that there may be a wider range of sizes of the interacting clusters, and therefore a broader energy barrier distribution, relative to the nanoparticle crystals.

The fact that all three samples have similar zero field-cooled magnetization curves is somewhat surprising. Equation 1 shows that in the absence of an applied field, the energy barrier is given by $KV$. With interactions, this barrier would be modified, depending on the value of the local field. This would be expected to broaden the energy barrier distribution, and in fact all three zero field-cooled magnetization curves are broad. Because of the liquids surrounding the particles in the dilute dispersion and the nanoparticle crystals, the high temperature drop-offs could not be compared, since the particles moved after the solvents melted. However, in earlier measurements we found that nanoparticle crystals showed a slower rate of drop-off above the blocking temperature than arrays made from particles of comparable size [27]. This is consistent with the energetic stabilization that occurs with domain formation.
5. Conclusions
We investigated the magnetic behavior of three different kinds of assemblies of 8.5 nm Fe nanoparticles: dilute dispersions, arrays formed by evaporation of the dispersions, and nanoparticle crystals grown by slow diffusion of a poorly coordinating solvent. These samples were characterized by zero field-cooled magnetization, remanent hysteresis loop, and magnetic relaxation measurements. The average spacing between the particles was determined from a combination of transmission electron microscopy and small angle x-ray scattering. In the arrays the spacing was 2.5 nm between the edges of the particle cores, while in the nanoparticle crystals the particles were more tightly packed, with a separation of 1.1 nm. The scattering measurements demonstrated that the length scale of the ordering, on average, was much greater in the nanoparticle crystals.

The reduced separation increased the magnetostatic interaction strength in the nanoparticle crystals, which showed distinctly different behavior in the rate of approach to saturation in the remanent hysteresis loops, and in the faster rate of time-dependent magnetic relaxation. Normally remanent hysteresis loops eliminate rotational contributions, because the particle moments must revert to lie along one of the easy axes at zero applied field. Because the Fe particles have six orthogonal easy axes, regardless of the direction of the local magnetostatic field, an easy axis direction is not far off. In the evaporated arrays, the combination of a relatively weak magnetic field and only short range structural ordering causes the assemblies to behave like a cluster glass, in which clusters of particles are strongly coupled with each other, but only moderately coupled to other clusters. Because there is a range of cluster sizes, the rate of magnetic relaxation is slower than in a dilute dispersion. The nanoparticle crystals of 8.5 nm Fe particles with 1.1 nm edge-to-edge spacing showed much stronger collective behavior, and at low temperature (10 K) may be viewed as dipolar ferromagnets. Efforts to determine the length scale of the magnetic correlations using small angle neutron scattering are underway.

Acknowledgments
S A M thanks the United States National Science Foundation (CTS-0227645), and the Petroleum Research Fund of the American Chemical Society (ACS-PRF-37578-AC5) for financial support.

References
[1] Murray, C B, Kagan, C R and M G. Bawendi, M G, 1995 Science 270 1335.
[2] Whetten, R L, Shafigullin, M N, Khoury, J T, Schaaff, T G, Vezmar, I, Alvarez, M M and Wilkinson, A, 1999 Acc. Chem. Res. 32 397.
[3] Sun, S, Murray, C B, Weller, D, Folks, L, and Moser, A, 2000 Science 287 1989.
[4] Luo, W, Nagel, S R, Rosenbaum, T F, and Rosensweig, R E, 1992 Phys. Rev. Lett. 67 2721-2724.
[5] Genc, Sand P. P. Phule, P P, 2002 Smart Mater. Struct. 11 140-146.
[6] Poddar, P, Wilson, J L, Srikanth, H, Yoo, Y-H, Wereley, N M, Kotha, S, L. Barghouty, L and Radhakrishnan, R, 2004 J. Nanoscience and Nanotechnology 4 192.
[7] Chantrell, R W, Fearon, M. and Wohlfarth, E P, 1986 Phys. Stat. Sol. (a) 97 213
[8] O'Grady, K, El-Hilo, M and Chantrell, R W, 1993 IEEE Trans. Magn. 29 2608
[9] Zhang, J, Boyd, C and Luo, W, 1996 Phys. Rev. Lett. 77 390
[10] Djurberg, C, Svedlindh, P, Nordblad, P, Hansen, M F, Bødker, F and Mørup, S, 1997 Phys. Rev. Lett. 79 5154
[11] Mørup, S, Madsen, M B, Frank, J, Villadsen, J and Koch, C J W, 1983 J. Mag. Mag. Mat. 40 163
[12] Jonsson, T., Nordblad, P, and Svedlindh, P, 1998 Phys. Rev. B 57 57
[13] Dormann, J, Bessais, L and Fiorani, D, 1988 J. Phys. C 21 2015
[14] Mørup, S and Tronc, E, 1994 Phys. Rev. Lett. 72 3278
[15] Held, G A, Grinstein, G, Doyle, H, Sun, S and Murray, C B, 2001 Phys. Rev. B 64 012408
[16] Russier, V, Petit, C, Legrand, J and Pileni, M P, 2000 Phys. Rev. B 62 3910
We have noted that over the course of two years in solution, the shape of the particles changed, becoming more faceted due to Ostwald ripening.