J Nanopart Res (2012) 14:1061
DOI 10.1007/s11051-012-1061-8

RESEARCH PAPER

Uniform growth of clusters of magnetic nanoparticles in a rotating magnetic field

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Received: 17 February 2012 / Accepted: 12 July 2012 / Published online: 31 July 2012

Abstract It was recently shown that the exposure of magnetic microbeads to a homogeneous magnetic field, which rotates around the axis perpendicular to the field direction, generates highly ordered two-dimensional particle arrays. In this work, the impact of downscaling such systems is analyzed. Dilutions of cobalt nanoparticles with an average diameter of 6 nm were brought into a rotating homogeneous magnetic field. A strong localization of the number of particles within a certain cluster size can be observed if the rotation frequency is adjusted to a specific particle concentration. In particular, we obtain an increase of 85 % of the maximum of the cluster size distribution, when changing the rotation frequency of the magnetic field from 300 to 750 rpm for a cobalt concentration of 35.95 mmol/l. We propose a heuristic model to explain the observed frequency dependence.

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Keywords Magnetism · Nanoparticles · Assembly · Growth mechanism · Agglomerates

Introduction

Magnetic nanoparticles have a wide range of possible applications in the field of spintronic devices and allow for the design of new nano-scaled components. Example of the many fields of research can be found in harddrive technology (Moser et al. 2002; Sun 2006), magnetic field sensors, or printable sensor designs (Weddemann et al. 2010a) which are based on granular magnetoresistive effects. However, all these new technologies require highly ordered particle monolayers or higher dimensional superstructures to allow for the accurate evaluation of the device signal and to guarantee the functionality of the components.

It was recently shown that highly ordered long-ranged superstructures of magnetic microbeads can be obtained by the exposure of such particles to a homogeneous magnetic field which rotates around the axis perpendicular to the field direction (Weddemann et al. 2010b). Within these systems, magnetoresistive effects cannot be observed since the typical distances between individual magnetic nanocores exceed the spin diffusion lengths due to the present size scales. Therefore, such microbeads may not be employed for the design of the above-mentioned spintronic devices.

It is not immediately possible to conclude from the success of the approach on the microscale to a similarly enhanced ordering effect on the nanoscale. Different physical aspects dominate the interaction process due to the different geometrical length scales involved. On the microscale, magnetic forces and steric repulsion are the main driving forces within the system (Petousis et al. 2007). In the case of nanoscaled ensembles, these contributions are superposed by the short-ranged van der Waals interactions and thermal contributions. However, it is well known that a stationary magnetic field strongly impacts the long range ordering of assemblies of magnetic nanoparticles (Weddemann et al. 2010a; Kim and Park 2010). Therefore, the approach of applying a rotating magnetic field for the creation of highly ordered monolayers remains a promising candidate for the creation of highly ordered assemblies of magnetic nanoparticles.

In order to validate such an approach on the nanoscale, similar experiments as reported in (Weddemann et al. 2010b) were conducted at different field rotation frequencies and particle concentrations.

Experimental section

For the experiments, magnetic nanoparticles were realized in a thermolysis procedure originally introduced by Puntes et al. (2001) A tenside mixture of 10 µl oleic acid and 40 µl oleylamine were heated to reflux in 1,2-dichlorobenzene. Afterward, a mixture of 100 mg of the precursor cobalt carbonyl and 2 ml dichlorobenzene was added in an iterative procedure to reach larger nanoparticles (Hütten et al. 2004). The resulting Co nano colloids have an average diameter of 6 nm, a standard deviation of 1.14 nm, and are crystallized in the ε-Co phase. For the experiments, two cobalt concentrations were employed given by $c_{\mathrm{low}} = 3.66$ mmol/l and $c_{\mathrm{high}} = 35.95$ mmol/l. The value choice leads to different dominating driving forces as will be shown later on. Further, all experiments were conducted at room temperature. Samples were prepared by placing a droplet of 1 µl of particle suspension on a SiO_2-substrate and exposing the sample to the rotating magnetic field until total evaporation of the carrier liquid. The magnetic field was realized by a magnetic stirrer RCT classic (IKA) as schematically shown in Fig. 1. The field strength is given by 500 Oe, rotation frequencies were chosen as

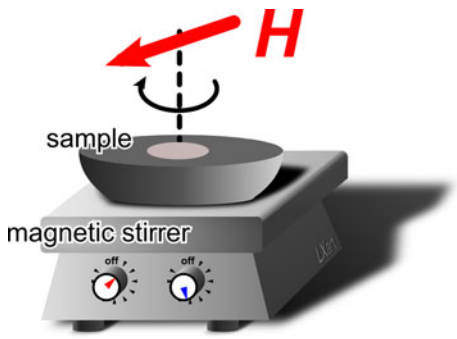

Fig. 1 Schematic representation of the employed magnetic stirrer setup

300, 500, and 750 rpm. Reference samples without an external magnetic field were realized to estimate the effect of van der Waals interaction and thermal contributions.

Results and discussion

A quantitative analysis of 40,492 and 15,086 particles in the low and high concentration reference sample, respectively, reveals the data shown in Fig. 2. The plot shows the ratio of particles which agglomerated in a certain cluster size class. The relation between cluster size and number of nanoparticles shows a similar characteristic (positions of local extrema) for the two different concentrations. A slightly stronger developed maximum and a decreased number of small clusters can be found for the concentration c_{high} which could be attributed to the higher number of particles

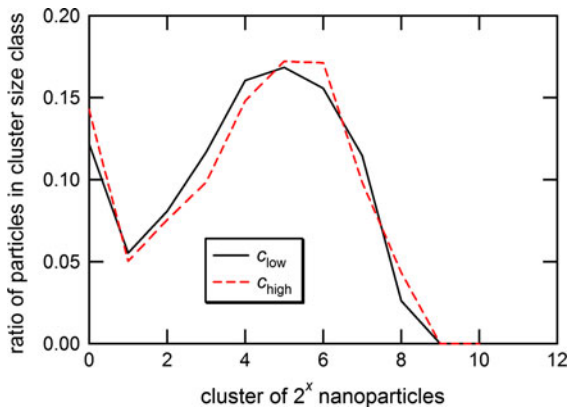

Fig. 2 Ratio of particles in a certain cluster size class without the application of an external magnetic field

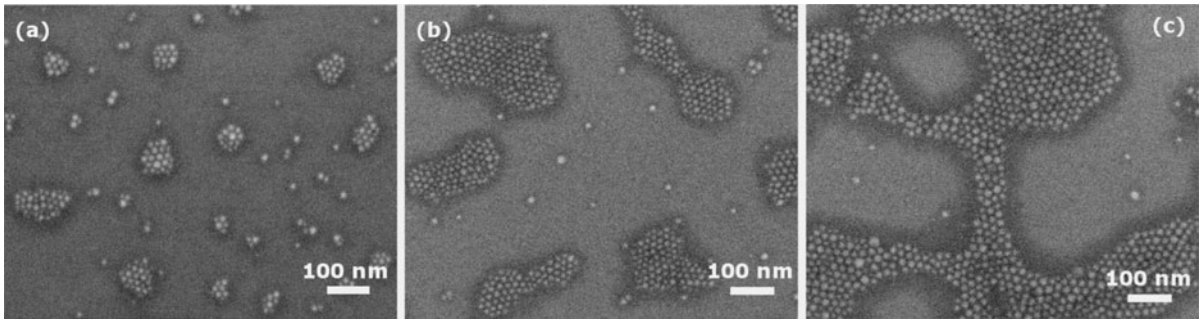

Fig. 3 SEM images of particle samples realized with a rotating homogeneous magnetic field of field strength 500 Oe and rotation frequency $f = 300$ rpm for **a** c_{low} and **b, c** c_{high}

which entail less free sample space and, therefore, an increased tendency to form agglomerations. On the contrary, an increasing number of individual particles can be found for c_{high}. However, under the assumption of an error approximately given by 5 % of the absolute number of particles per class due to the manual counting procedure, such conclusion is not possible at this point. In order to analyze the effect of a magnetic field, samples of both concentrations were exposed to a rotating magnetic field parallel to the sample plane with the rotation axis perpendicular. Examples of samples created under the influence of the magnetic field are shown in Fig. 3. Such pictures were evaluated in a similar procedure as before for the evaluation of the reference samples.

The results shown in Fig. 4 represent the data obtained by analysis of about 20,000 particles each. For the low concentration c_{low}, an increased development of the maximum within the distribution can be found toward lower values of the rotation frequency applied. Also, a significant decrease of the number of single particles may be reported in this case. Therefore, at this stage, it may already be concluded that the magnetic field entails an enhanced ordering effect: the cluster growth appears to be more homogeneous which results in a lower deviation in the cluster size distribution. On the other hand, an extrapolation of this data trend would suggest that the highest localization of cluster sizes is reached if a stationary magnetic field (see e.g., Kim and Park 2010 or Weddemann et al. 2010a) is employed.

This assumption proves wrong if the data of the highly concentrated dilution are considered which show an opposite trend in regards to the behavior of the maximum. Again, a significant decrease of single particles and small clusters is observed. In contrast to the low concentration, the maximum is more developed when the higher field frequency is chosen. This is in contrast to the situation above and gives evidence

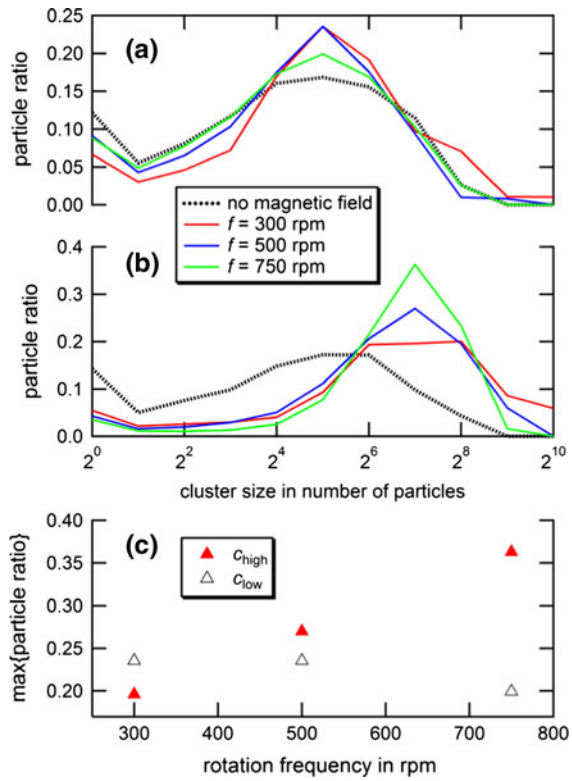

Fig. 4 Particle ratio of particles in a certain cluster size class under the influence of an external magnetic field for the field frequencies 300, 500, and 750 rpm and concentrations **a** c_{low} and **b** c_{high}. The data represent the analysis of approx. 20,000 particles per plot. **c** Different frequency dependence of the maximum particle ratio of the distributions can be observed for c_{low} and c_{high}. (Color figure online)

that the ordering dynamics differ from those in the case where the magnetic field is set stationary. The difference may already become evident when inspecting the resulting structures shown in Fig. 3. A homogeneous magnetic field results in a long-ranged ordering, whereas the rotating setup entails a local one in the sense that clusters of similar particle numbers are formed.

In order to understand the observed behavior, the similar cluster characteristics of the reference samples need to be reviewed again. The very slight alteration in the cluster size distribution for the two concentrations is due to the short range of the attractive van der Waals interaction which decays $\sim d^{-6}$ with d the distance between contiguous, interacting particles. On long distances, particles move randomly because of thermal contributions, and agglomerate if they approach each other. The thermal motion of such particle clusters is reduced due to the increased size of the confined objects, and the cluster stops to move. In principle, this is similar to the nucleation process according to the LaMer model (LaMer and Dinegar 1950) where nucleation seeds can only be formed in areas where the concentration exceeds a critical threshold. For higher concentrations, such a condition is met in more places along the sample which results in a slightly more developed maximum and in less single particles remaining after the agglomeration process. However, once a small cluster is formed, the surrounding area within the attraction range of the van der Waals potential no longer contain free particles and, therefore, the cluster cannot grow any further. Consequently, both distributions resemble only the characteristic of randomly distributed particles and, thus, reveal a similar behavior.

The interaction of particles via their dipolar magnetic stray field introduces a long-ranged force. Even though the magnetic coupling is usually much stronger than thermal contributions, it is superimposed by van der Waals interactions on short distances (Lalatonne et al. 2004). Also, the magnetic moment vector of individual particles will no longer follow the external field direction, once van der Waals contributions become important because at these length scales magnetic particle–particle couplings exceed external magnetic contributions. Therefore, a system reaches its equilibrium state once all van der Waals driven dynamics are finished, and the impact of the enhanced ordering effect is higher; more time is required to reach this state. This simple heuristic model of the nano dynamics allows understanding the findings shown in Fig. 4.

For high frequencies, the time intervals between attractive and repulsive magnetic forces are very short. Interacting particles oscillate close to their initial position (Cebers and Ozols 2006) and thermal contributions are the driving force to initiate cluster formation. Therefore, the situation resembles the state of the reference samples. An example for this type of behavior can be found for the low concentration sample at a rotation frequency $f = 700$ rpm (Fig. 4a, green line). A decrease of the applied rotation frequency results in an increased time for particles to interact attractively. It was shown by Rinn et al. (1999) that this may be described as contribution to an effective diffusivity which results in a higher standard deviation of the distances particles travel over time. Therefore, particles move through larger regions of the sample and the probability for two particles to agglomerate is increased. Such tendency can be found in Fig. 4a, blue to red line. However, it may seem surprising that the average cluster size is not significantly increased. Instead a decrease of small clusters and, consequently, a decrease of the standard deviation is the result. The reason for this behavior lies in the increased regions that single particles and small clusters pass during the agglomeration process. Thus, the cluster characteristics resemble an average number of particles taken along a specific sample area which increases with decreasing frequency. Local fluctuations are smoothed out and a homogeneous cluster growth is the result.

The employed terms of high and low frequencies are not fixed values but depend on the average distance between contiguous particles or, in other words, on the particle concentration. The high concentration sample is, therefore, an extension of the first experiment into the regime of very low frequencies. For the data shown in Fig. 4b analogous explanations hold. With the strongly reduced inter-particle distances, the agglomeration process due to magnetic coupling is accelerated, and cluster of high particle number are formed on very short time scales. The long range of the magnetic fields results in an attraction of particles over longer distances which results in a very low number of single particles. Once the first cluster has formed, individual moments align their magnetic vectors in a way to minimize the total moment of the cluster which entails

magnetically inert objects (Mørup et al. 2010). In contrast to the situation above, a higher frequency results in an increased standard particle mobility during the agglomeration phase. Therefore, high frequencies entail a homogeneous cluster growth (Fig. 4c). In particular, the maximum of the distribution for the concentration c_{high} increases about 85 % if a frequency of 750 rpm instead of 300 rpm is employed.

Conclusion

We may conclude that the exposure of magnetic nanoparticles to a rotating homogeneous magnetic field results in an increased ordering effect, which is in contrast to a stationary field of local nature. The adjustment of the field frequency allows for a uniform cluster growth.

Acknowledgments The authors would like to thank the SFB 613 and the FOR 945 for financial support in the framework of the project K3 and project 3, respectively. Alexander Weddemann gratefully acknowledges financial funding from the Alexander von Humboldt foundation.

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