# Flux closure in two-dimensional magnetite nanoparticle assemblies

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Magnetic force microscopy and spectroscopy are used to study two-dimensional islands of spherical 21-nm magnetite nanoparticles. The observed repulsion of the magnetic tip at the edges of the islands is a clear sign of magnetic ordering: strong magnetic dipole-dipole interactions cause blocking of the nanoparticle dipole moments. These moments will be shown to form flux-closure structures, which is the origin of the magnetic contrast in dense two-dimensional magnetic nanoparticle assemblies.

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## INTRODUCTION

Highly controllable, magnetic nanoparticles are widely studied because of their potential use in applications such as magnetic storage devices and in biomedicine. In present-day, high-density hard disks the information is stored in thin films consisting of nanometer-sized, arbitrarily shaped magnetic grains.[1] A single bit on a hard disk corresponds to a large group of grains with their magnetic moments aligned. Since the collection of grains is dense, their magnetic moments may interact; such interactions have an important effect on the magnetic properties of the thin film such as its coercive field. For applications in biomedicine, on the other hand, the magnetic nanoparticles need to be covered with specific biological molecules. They can then be used for labeling cells, drug delivery, heating tumors (hyperthermia), and contrast enhancement for magnetic resonance imaging.[2] The magnetic properties of the individual particles and their mutual magnetic interactions determine the possible application of these systems.

Advanced chemical preparation methods can be used to produce magnetic nanoparticles with precisely controllable composition, shape, and size, and a high degree of crystallinity.[3,4] A thin-film assembly of such particles can serve as an (almost) ideal model system for studying the mutually interacting magnetic nanoparticles. Because of its nanoscale dimensions, each nanoparticle consists of only a single domain with a relatively large magnetic dipole moment. When sufficiently small, the particles become superparamagnetic, which means that their magnetic moments are virtually free to rotate. In a dense collection of nanoparticles, the magnetic dipole moments of the individual particles strongly interact. Three-dimensional (3D) systems like ferrofluids have been studied with a variety of techniques such as (zero) field cooling magnetization, resonant magnetic x-ray scattering, and Mössbauer spectroscopy.[5–9] Magnetic dipole-dipole interactions have been shown to change the relaxation time of magnetic moments and to cause spin-glass behavior.[10–13] Recently, high-quality two-dimensional (2D) assemblies of magnetic nanoparticles have been prepared by drop casting and by the Langmuir Blodgett technique.[14,15] For cooled samples with arrays of 8.5-nm magnetite ($Fe_3O_4$) particles, magnetic susceptibility measurements have shown strong dipolar coupling between the nanoparticles.[11] In a recent magnetic-force-microscopy (MFM) study of a 2D assembly of spherical 12-nm Co nanoparticles,[16] the existence of correlated areas with diameters of at least ten nanoparticles was demonstrated and attributed to dipolar coupling between the nanoparticles. The configuration of the magnetic moments in these correlated regions however is not yet clear.

We present a study of a 2D model system consisting of monodisperse magnetite nanoparticles. With a combination of MFM and magnetic force spectroscopy (MFS), we image the magnetic force across the 2D islands of nanoparticles. While above the islands the interaction is purely attractive, we find repulsive forces at the edges of the islands showing the presence of magnetic ordering. The experimental results are supported by numerical simulations which show a strong tendency for flux closure within the 2D islands.

## EXPERIMENTAL RESULTS

Two-dimensional arrays of 21-nm magnetite nanoparticles[17,18] were prepared by drop casting on graphite.[19] The sample was subsequently introduced into a UHV setup.[20] Noncontact atomic force microscopy (nc-AFM) was used in constant frequency-shift mode to study the topography of the surfaces. MFM measurements were subsequently performed in constant-height mode with the magnetic tip lifted to 70 nm above the substrate, which means to approximately 45–50 nm above the islands of nanoparticles (taking into account the layers capping the particles). For a distance of 60 nm above the substrate (respectively, 35–40 nm above the islands) similar results were found. We chose for these lifting heights to be sure that the magnetic forces dominate the shorter range van der Waals forces. All measurements have been performed with constant amplitude in the range of 50–100 nm. The contact-potential difference between tip and sample was corrected for by applying an appropriate potential. The experiments have been carried out at room temperature, unless otherwise stated. In addition to the imaging experiments, MFS was carried out at specific positions on the surface: the *x*-*y* scan was interrupted and the frequency shift *df* was measured as a function of the distance to the surface. Since the oscillation amplitudes are similar to the characteristic length scale of the interaction, the obtained frequency shifts are in fact proportional to the forces.[21] This means that positive frequency shifts corre-

 

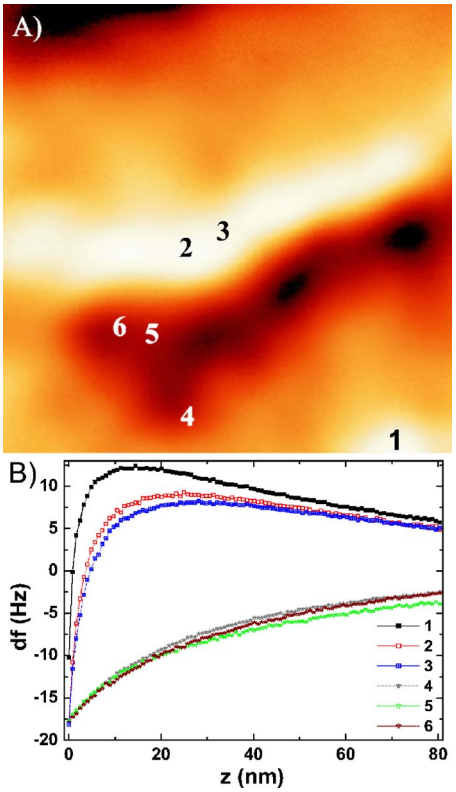


FIG. 1. (Color online) (a) MFM image of a $1\times1$ $\mu m^2$ area of a hard disk (200 Mbit/cm$^2$ showing one of the elongated structures (partly attractive and partly repulsive). The vertical scale ranges from −6 Hz (dark; attractive) to 6 Hz (bright; repulsive). (b) MFS curves measured at the positions indicated. $z=0$ corresponds to the distance where the feedback set of the AFM measurement is reached (−15 Hz). Curves 1, 2, and 3 show repulsion for distances larger than a few nanometers; curves 4, 5, and 6 attraction for all distances.

spond to *repulsion* between tip and sample, negative frequency shifts to *attraction*.

We first carried out MFM and MFS on a small piece of a longitudinal storage medium (hard disk; 200 Mbit/cm$^2$) to test the performance of the magnetic tip. In the MFM image the well-known elongated structures were clearly visible with alternating areas of attraction and repulsion. Figure 1 shows part of one of these elongated structures as well as MFS curves measured at specific positions. MFS curves taken in the dark area clearly show that the interaction is attractive for all distances; in the bright area, the curves show that the interaction is repulsive for distances larger than a few nanometers. The forces are long range (up to at least 100 nm) and originate in the interaction of the magnetic moment of the tip with the stray fields of the magnetic domains written on the hard disk. Only for the smallest distances does the van der Waals interaction between tip and sample become dominant resulting in strong attraction.

Typical AFM and MFM results for the sample with the 2D assembly of 21-nm magnetite nanoparticles are shown in Figs. 2(a) and 2(b), respectively, the inset taken at higher resolution shows the individual particles. In the MFM image, the islands of nanoparticles show up as dark-colored areas

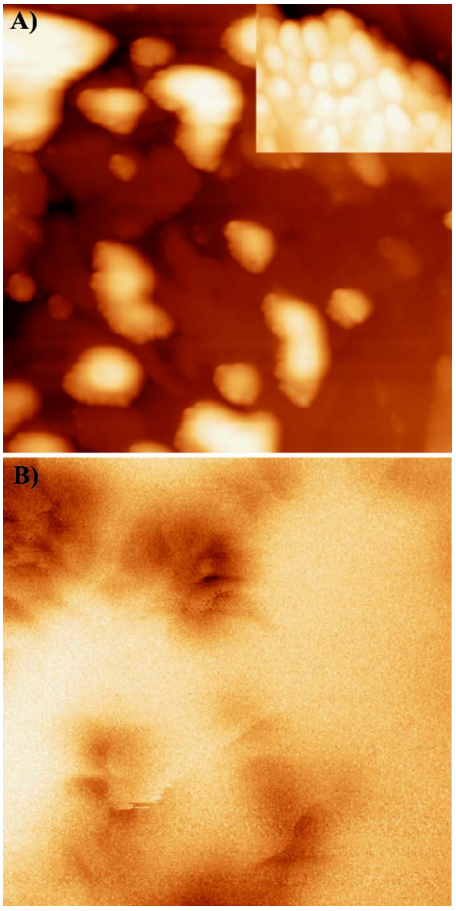


FIG. 2. (Color online) (a) AFM image of a $1\times1$ $\mu m^2$ area of an HOPG surface with 2D islands consisting of 21-nm spherical magnetite nanoparticles (bright areas). The vertical scale ranges from 0 nm (dark) to 45 nm (bright). Most of the islands consist of a monolayer; only the one in the topmost left corner is a double layer. The inset shows a higher resolution AFM image with clearly resolved individual particles (area $0.17\times0.13$ $\mu m^2$; measured with a nonmagnetic tip). (b) MFM image of the same area. The vertical scale ranges from −5 Hz (dark) to 0 Hz (bright). The dark areas correspond to the 2D islands of nanoparticles. Note that on top of the islands magnetic contrast is present.

with small contrast (negative frequency shifts), reflecting attraction. We observed attraction above all islands, for this sample as well as for other samples. The attraction between tip and island can be understood in terms of the relatively strong magnetic field of the tip, magnetizing the nanoparticles. This effect is expected to take place predominantly during the AFM scans while the tip-surface distance is small. Some of the structures present in the MFM image seem to be too abrupt to originate in the magnetization structure. They may be related to magnetic changes during the scans, although it should be noted that all structures reproduce very well in subsequent measurements taken at a height of 60 nm.

From the MFM images it seems that the interaction between tip and surface is always attractive. Employing MFS, however, we will show that in specific areas repulsion is present. An AFM image of the surface area studied is shown in Fig. 3(a); MFS curves taken at the positions indicated are shown in Fig. 3(b). The results were acquired at 90 K, simi-

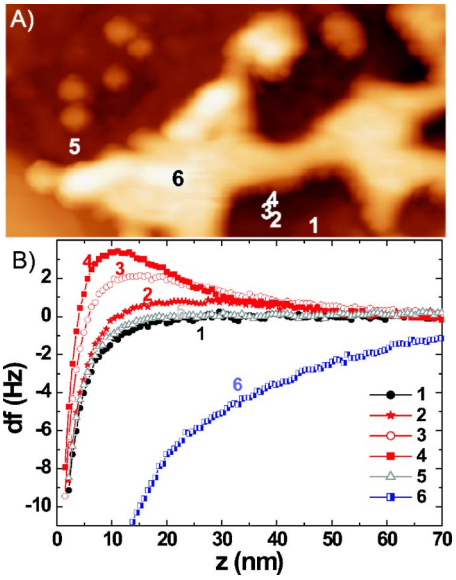


FIG. 3. (Color online) AFM image ($0.5\times1$ $\mu m^2$ area) of same sample as in Fig. 2, showing a large island of nanoparticles. The vertical scale ranges from 0 nm (dark) to 45 nm (bright). (b) MFS curves measured at the positions indicated. $z=0$ corresponds to the distance where the feedback set of the AFM measurement is reached (−17 Hz). Curves 2–4 clearly show repulsion (positive frequency shifts), curves 1, 5, and 6 only attraction (negative frequency shifts).

lar results were obtained at 300 K. Curve 1, taken above the highly oriented pyrolitic graphite (HOPG) surface, shows attraction for all distances due to van der Waals forces. Curve 6, taken on top of the island, also shows attraction but with a much weaker distance dependence. This long-range behavior agrees well with the tip magnetizing the nanoparticles, resulting in attractive dipole-dipole interactions. Curves 2–4 were measured at the edge of the island. Surprisingly, the interaction is predominantly repulsive, with the repulsion becoming stronger when approaching the island. We observed such repulsive magnetic forces at the edges of many islands. Note that the interaction at the edge of an island is not always repulsive (see curve 5). The repulsive curves show that the frequency shifts are small for large $z$, explaining why repulsion is not visible in the MFM image taken at a height of 70 nm [Fig. 2(b)].

Obviously, with the tip laterally sufficiently far away, the field exerted by the tip is weak and the magnetic moments of the nanoparticles are blocked. Since the coercivity of the individual nanoparticles is small,[18] this is probably caused by the strong magnetic dipolar coupling between the nanoparticles.[11] Each nanoparticle has a magnetic moment of $2.2\times10^{-18}$ $Am^2$, as determined by the analysis of magnetization curves measured for dilute dispersions in an organic solvent. For two particles next to each other, with an interparticle spacing of 3 nm and their magnetic moments aligned in the head-to-tail configuration, the magnetic dipole-dipole energy amounts to about −110 meV per particle (see also Ref. 22). For a 2D island of nanoparticles, the dipoles are oriented such as to minimize the total energy. This explains our observations: An approaching magnetic tip may be repelled since, for reorientation of the dipoles, an energy barrier has to be overcome.

## NUMERICAL SIMULATIONS AND DISCUSSION

To study the magnetic dipolar interactions in a more quantitative way, we performed Monte Carlo simulations on an arrangement of 31 nanoparticles [see Fig. 4(c)]. This arrangement was taken to be close to the experimental one shown in the inset of Fig. 2(a). Starting with an arbitrary configuration of magnetic dipoles, i.e., with their moments pointing in any direction *in* as well as *out* of the plane of dipoles, their directions were varied while minimizing the total energy. The total energy was taken as the sum of the magnetic dipole-dipole energies of all pairs of particles with, for the individual moments, the experimentally determined value. The simulations were carried out at room temperature

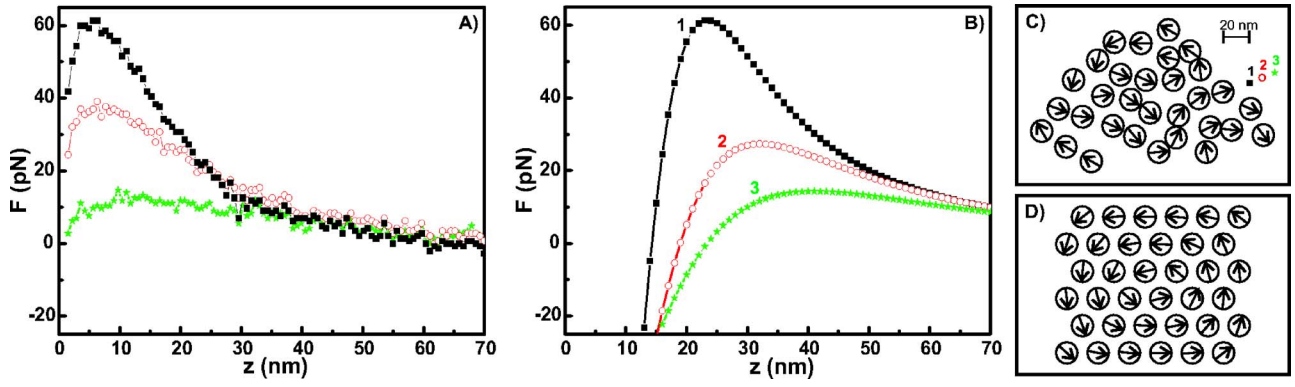


FIG. 4. (Color online) (a) Experimental *magnetic* force-distance curves obtained from curves 2–4 in Fig. 3 (same symbols used for corresponding curves). (b)–(d) Results of Monte Carlo simulations. Ordered arrangement of nanoparticles is shown in (d), with arrows indicating the calculated direction of the magnetic dipoles and illustrating the importance of flux closure. The configuration of moments of a slightly disordered arrangement of nanoparticles [(c); similar as experimental arrangement as inset in Fig. 2(a))] is also predominantly determined by flux closure. This configuration has a total energy of −20.3 eV. In (b) force-distance curves for the "frozen" configuration of dipoles are shown, calculated at the positions indicated in (c); as in the experiments, repulsion increases upon lateral approach of the 2D arrangement of particles. The horizontal shift between the curves in (a) and (b) is caused by different definitions of $z=0$ (see text).

and showed that different final configurations may be reached that correspond to slightly different local energy minima. For all final configurations we found that the dipoles are all oriented in the plane of the nanoparticles. One of the simulated configurations is shown in Fig. 4(c). It is obvious that large correlated areas with all magnetic moments aligned are not present. It rather seems that, with many dipoles in the head-to-tail configuration, flux closure plays an important role. Note that, since the magnetic energy per particle amounts to about −650 meV, the simulated configuration is very stable with respect to thermal excitation. To study the role of flux closure and disorder in more detail, we performed a Monte Carlo simulation on a regular hexagonal arrangement of 36 nanoparticles. The results are shown in Fig. 4(d) and clearly illustrate that flux closure in fact determines the orientation of the dipoles. For slightly disordered arrangements [Fig. 4(c)] of up to 100 nanoparticles, we found that the largest areas with the moments aligned consist of not more than ten nanoparticles. The dimensions of these correlated areas are similar to those with different contrast observed in the MFM experiment [Fig. 2(b)]. It therefore seems plausible that these experimental regions have the same origin, i.e., they are part of flux-closure structures. The correlated areas observed in a compact monolayer film of Co nanoparticles[16] are likely to be caused by the same mechanism.

We now consider the interaction of the magnetic tip with the magnetic moments of the nanoparticles. The Monte Carlo simulations are set up for a static arrangement of dipoles and it is not straightforward to include the moment of the oscillating tip. We simply assume that the configuration of dipoles corresponds to the calculated one without the tip [Fig. 4(c)] and that it is "frozen," i.e., that it is not influenced by the presence of the tip. At the edge of the island, with the tip sufficiently far away, this is expected to be a good assumption: The stray field of the tip is so small that the configuration of dipoles will remain in the same local energy minimum. In Fig. 4(b), we show force-distance curves for a magnetic tip (dipole moment pointing down) interacting with the "frozen" configuration. The force arises from the interaction of the dipole moment of the tip with the stray magnetic fields of the nanoparticle dipoles. Clearly, the interaction is dominated by repulsion. For comparison, three of the measured repulsive curves are shown in Fig. 4(a). The curves were first converted to force-distance curves[21] and subsequently corrected for the van der Waals forces by subtracting the curve obtained above the HOPG substrate. The resulting curves therefore correspond to magnetic forces. Measured and simulated curves agree quite well: Not only does repulsion increase when the tip laterally approaches the nanoparticles, also the range of the magnetic forces is similar. The horizontal shift between measured and simulated curves is caused by different definitions of $z=0$: for measured curves a certain frequency shift and for simulated curves the plane of dipoles. The only free parameter in the simulations is the magnetic moment of the tip, for which we used $2.4 \times 10^{-16}$ Am$^2$. Considering the apex of the tip and the magnetic material used, this value is reasonable. Force-distance curves were also calculated for other lateral positions at the edge and, as in the experiments, some curves show very small magnetic interaction. On top of the islands, on the other hand, the assumption used is not valid: The experimentally observed attraction shows that for small $z$ the field of the tip is so strong that the configuration is "pushed" out of its minimum (i.e., the equilibrium position *without* tip). To model this properly is more complicated since it is *a priori* not clear whether or not the moments of the individual nanoparticles are able to follow the oscillating tip.

As a test of the proposed model we performed further experiments on 2D islands of significantly smaller magnetite nanoparticles (physical diameter 10.8 nm; magnetic diameter 9.4 nm). The maximum dipolar energy of two particles separated by 3 nm decreases to about −8.5 meV per particle. This energy is small compared to $k_BT$ at room temperature and dipolar coupling should not play any role. In the experiments, different islands were studied and repulsion was never observed, as expected.

## CONCLUSIONS

In summary, we have shown that MFS gives detailed information on the interactions between magnetic nanoparticles in a dense 2D assembly. The observed repulsion between tip and nanoparticles shows that dipolar coupling between the particles causes blocking of their magnetic moments. The experimental observations agree well with numerical calculations, which show that the magnetic moments arrange themselves in flux-closure structures. Such structures have been identified in the MFM images and are likely to be the cause of previously observed magnetic contrast in dense 2D magnetic nanoparticle assemblies. The results open up the way to more-quantitative studies of yet unexplored phenomena, such as thermal stability of magnetic order in 2D systems, effect of size and arrangement of nanoparticles on magnetic order, and response time of nanoparticle moments to an oscillating tip.

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[19] Spherical magnetite nanoparticles were prepared by chemical reduction of iron acetylacetonate in organic solvent; they were capped with oleic acid and oleylamine and have a narrow size distribution (polydispersity 10%; see also Ref. 18). The magnetic diameter of the particles is slightly smaller than the physical diameter (18.4 nm instead of 21 nm), as determined by the analysis of magnetization curves measured for dilute dispersions in an organic solvent. The particles were deposited by placing a known volume of the nanocrystal dispersion in hexane on atomically flat HOPG (highly oriented pyrolytic graphite), followed by solvent evaporation (drop casting).
[20] The ultra-high-vacuum system has a base pressure of better than $1 \times 10^{-10}$ mbar and is equipped with an OMICRON VT AFM/STM. Except for the higher-resolution measurent, all experiments have been carried out with a commercially available conducting cantilever (resonance frequency about 70 kHz; cantilever constant 1.8 N/m) with a magnetic tip (Si tip with apex radius of about 25 nm covered with a 40-nm thick CoCr film).
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