Internal magnetic structure of dextran coated magnetite nanoparticles in solution using small angle neutron scattering with polarization analysis

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For many applications, the internal magnetic domain structure of magnetic nanoparticles may play a critical role in the determination of their collective magnetic properties. Here we utilize polarization analyzed small angle neutron scattering (PASANS) to study the individual magnetic morphologies of an interacting aqueous Fe_3O_4 nanoparticle system. Our results demonstrate that the total magnetic moment of the colloid is randomized, as expected in low fields, while the nuclear structure is anisotropic. Model fits indicate that the magnetic domains within the nanoparticle core at 1.5 mT have dimensions that approximate those of the structural grains perpendicular to the field, but the domains extend over multiple grains along the field direction. The asymmetry in the magnetic domain formation in weak fields undoubtedly contributes to the magnetic anisotropy and thus to the enhanced heating reported for hyperthermia applications of these systems. (© 2011 American Institute of Physics. [doi:10.1063/1.3540589]

Magnetic nanoparticles can be found in applications ranging from ordered nanoparticle arrays for data storage¹ to biomedical applications (like magnetic resonance imaging contrast agents,² hyperthermia for cancer treatment,³ and cell sorting⁴) to magnetorheological fluids for shock absorption.⁵ Understanding the critical parameters of the magnetic nanoparticle system for each application is the subject of intense research. Given the size range available, from 10 nm up to several micrometers, the internal magnetic structure of a single nanoparticle can be expected to play a crucial role in optimizing these parameters. This is especially important near the transition from a single magnetic domain to multiple magnetic domains, which are approximately 20–120 nm for most magnetic systems.

There exists a number of methods for imaging magnetic domains⁶ over the micrometer to nanometer scale, including magnetic force microscopy; magneto-optical Kerr effect; spin-polarized scanning tunneling microscopy; neutron scattering; and x-ray and electron microscopy techniques (such as x-ray magnetic circular dichroism, photoemission electron microscopy, and Lorentz and Fresnel imaging). Resolving the internal magnetic domain structure of magnetic nanoparticles requires subnanometer resolution, and so the most commonly used techniques are based on electron microscopy. Unfortunately, this limits the number of particles that can be examined, preventing the formation of useful statistics about the nanoparticle system as a whole. In contrast,

x-ray and neutron techniques⁷ provide ensemble averaging of the entire nanoparticle system while yielding the necessary resolution.

Our system is composed of core/shell nanoparticles dispersed in water with a concentration of about 20 mg/ml. The core is >98% Fe₃O₄ (determined by Mossbauer spectroscopy) with an average diameter of \approx 50 nm (Fig. 1), and it is coated with dextran to prevent agglomeration in solution. Though crystalline, the core is not a single crystal, but is composed of structural grains.³

Here we used polarization analyzed small angle neutron scattering (PASANS) at room temperature to examine the internal magnetic structure from a collection of magnetite nanoparticles in D₂O under an applied magnetic guide field of 1.5 mT. {Unpolarized neutrons were not sufficient for determining the magnetic structure because the magnetic signal is relatively weak when the nanoparticles are contrasted with H₂O, and the magnetic structure determination is ambiguous [Fig. 2(a)] when the nanoparticles are contrasted with D₂O.} The PASANS measurements were performed at the NIST Center for Neutron Research on the NG-3 beamline. To cover the Q range⁸ of (0.005-0.2) Å⁻¹, two different wavelengths of neutrons were used: (5 ± 0.6) Å and (7.5 ± 0.9) Å. The 5 Å (7.5 Å) neutrons were polarized with an efficiency of 0.888 ± 0.005 (0.935 ± 0.003) using an FeSi supermirror. The incident neutron polarization direction can be reversed using a flipper coil with an efficiency of 0.988 ± 0.004 (0.979 ± 0.003). After scattering from the sample, neutrons are analyzed⁹ by passing through a polarized ³He cell. The orientation of the ³He spin filter can also

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FIG. 1. (Color online) TEM image of Fe_3O_4 nanoparticle coated with dextran and cross-linked with a maleimide tail, which has no effect on the core.

be reversed with a nuclear magnetic resonance pulse. The data are then corrected for detector efficiency, background, and the polarization efficiency plus the time dependence of the ³He cell according to previously described methods.¹⁰

Measurement of all four neutron spin cross-sections (++, +-, -+, and --) allows for the unique separation of nuclear scattering (N^2) from magnetic scattering, irrespective of whether the sample is magnetically saturated. Simply, the (++) and (--) non-spin-flip scattering contains information about nuclear scattering and magnetic scattering, primarily from moments parallel to the applied field $(M_Y^2 = M_{PARL}^2)$, while (+-) and (-+) spin-flip scattering contains only magnetic scattering, including perpendicular moments (M²_{PERP}, which is a linear combination of M_X^2 and M_Z^2 . Starting from the efficiency-corrected two-dimensional (2D) scattering patterns with the magnetite nanoparticles in the 1.5 mT field parallel to the y axis, area-normalized sector slices¹¹ of $\pm 10^{\circ}$ are taken about specific θ angles of interest to extract angular information, where θ is the angle between the x axis (horizontal midline of the detector) and the projection of Q onto the X-Y detector plane [see inset to Fig. 2(b)]. In the case of anisotropic nuclear scattering (N^2) , angle independent measurements can be obtained from the angular asymmetries of the scattering equations.¹²

$$N_{\theta}^2 = \frac{A_{\theta} + \sqrt{A_{\theta}^2 - B_{\theta}^2}}{2} \tag{1}$$

where $A = (I^{--} + I^{++})$ and $B = (I^{--} - I^{++})$.

The clear decrease in N^2 intensity as a function of θ [Fig. 2(b)] highlights the need for angle independent analysis [Eq. (1)]. Additionally, the slope of N^2 varies as a function of Q. Both of these effects are consistent with the unpolarized SANS data [Fig. 2(a)]. Dynamic light scattering and x-ray powder diffraction³ show that each nanoparticle is composed of structural grains in the shape of parallelepipeds. Model fits to the previous unpolarized SANS data³ indicate that there are three characteristic dimensions of approximately 6.5 nm long, 19 nm wide, and 49 nm high. Our current data show that the N^2 scattering at $\theta = 0^\circ$ (perpendicular to the small field) has features at high Q that appear to originate from these individual parallelepipeds. In contrast, the high **Q** feature is less prominent in the N^2 scattering at $\theta = 90^{\circ}$, suggesting a possible preferential alignment of the long axis of the parallelepipeds parallel to the small field. In addition, the overall scattering intensity is weaker, suggesting that the scattering peak at $\theta = 90^{\circ}$ may be shifted to lower Q. This is consistent with structural anisotropy: the particles have a time-averaged, short-range (local) order along the field direction.

For consistency, since N^2 is anisotropic, we focus on $\theta = 0^\circ$ where the scattering intensity from N^2 and M_{PARL}^2 are maximized. Figure 3(a) clearly shows that there is magnetic scattering both parallel and perpendicular to the applied field. The intensities of these curves are similar at low **Q**. Therefore, we know that the magnetic moments are randomized in 1.5 mT, as expected. However, the magnetic scattering parallel and perpendicular to the field have very different shapes. Specifically, the magnetic scattering from moments parallel to the guide field falls off at a much lower **Q** (near 0.04 Å⁻¹). To



FIG. 2. (Color online) (a) Comparison of the circularly averaged unpolarized data with the total polarized data (nuclear and magnetic) to show that the shape of the data is similar. Note that the polarized data are scaled by an arbitrary factor to align backgrounds. (b) Plot of the nuclear scattering data as a function of sector angle.

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FIG. 3. (Color online) (a) The nuclear and magnetic data are shown on the same graph for direct comparison, with parallelepiped model fits of the magnetic scattering. (Note: Noise in the magnetic scattering parallel to the field impeded fitting at higher Q.) (b) Schematic of the magnetic moment orientation within the magnetic core. The dashed lines represent the long axis of the structural grains, and the arrows represent the local area magnetic moment (except for the arrow in the center labeled H, which represents the applied magnetic field).

quantitatively identify the differences between the two magnetic orientations, the data were fit [shown in Figs. 3(b) and 3(c)] using interactive IGOR models.¹³

First, we model the magnetic scattering as a polydisperse sphere to capture the critical sizes of the magnetic domains. The scattering corresponding to the moment parallel to the field can be described by a sphere of radius 15 nm, whereas the scattering corresponding to the moment perpendicular to the field can be described with a sphere of radius 7.5 nm. The model also highlights that the magnetic domains oriented parallel to the field are a factor of 4 larger than the magnetic domains oriented perpendicular to the field.

Then, we model [Fig. 3(a)] the magnetic domains as parallelepipeds for comparison with the structural grains. The dimensions of the magnetic domains parallel to the field are \sim 22, 32, and 70 nm, whereas the dimensions of the magnetic domains perpendicular the field are \sim 8, 15, and 70 nm. Again, these fits are very sensitive to the smallest length scale. The shortest dimension of the magnetic domains parallel to the field is approximately three times the shortest dimension of magnetic domains perpendicular to the field. (Note that the perpendicular magnetic domains have lengths that are similar to the dimensions of the structural grains.) Overall, the critical dimension for the magnetic domains is dictated by the high **Q** turnover and is the same regardless of the model chosen (\sim 8 nm for the magnetic domains perpendicular to the field and \sim 20 nm parallel to the field).

To reconcile the differences between the length scales determined from the magnetic scattering parallel and perpendicular to the guide field, one must remember that each nanoparticle is composed of a stack of parallelepiped structural grains. The orientation of these grains relative to the field is random {although the structural scattering [Fig. 2(b)] indicates a slight preferential alignment of the long axis parallel to the field}. Our data thus indicate that correlation lengths of the magnetic moments perpendicular to the field are significantly shorter than the correlation lengths of the magnetic moments parallel to the field [Fig. 3(b)]. In terms of the structural grains, it appears that the magnetic domains can be represented as a single structural grain for the component of the moment that is perpendicular, but domain sizes associated

with the component of the moment parallel to the field must extend over several structural grains. The contrast between the magnetic correlation lengths for moments parallel and perpendicular to the field is striking considering that the applied field is extremely weak (1.5 mT). Our results suggest that magnetic shape anisotropy is present within each nanoparticle.

In conclusion, PASANS investigations of Fe₃O₄ nanoparticles in solution have provided unexpected insight into the magnetic correlation lengths within a single nanoparticle as well as the structural anisotropy of the whole system. Our results demonstrate that the magnetic moment is random in low fields. However, the nuclear structure is anisotropic, presumably as a result of local nanoparticle alignment. Model fits indicate that the magnetic domains parallel to the field have dimensions that are approximately three to four times those of the magnetic domains perpendicular to the field direction. Relative to single domain particles under the same conditions, the strong asymmetry in the magnetic domain structure, even in very small fields, may give rise to the structural anisotropy in our nanoparticle solutions and undoubtedly contributes to the enhanced heating reported for hyperthermia applications of these systems.

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- ⁷Their limitation lies in the fact that you need high-power x rays or a high intensity neutron source that can only be obtained at specialized facilities.
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