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# Achieving a noninteracting magnetic nanoparticle system through direct control of interparticle spacing

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Monodisperse magnetite ( $\text{Fe}_3\text{O}_4$ ) nanoparticles (NPs) were synthesized and coated using a  $\text{SiO}_2$  shell with controlled thickness ranging from 3.0 to 20.0 nm. The temperature-dependent zero-field-cooled (ZFC) and field-cooled (FC) magnetizations of the 7.5 nm  $\text{Fe}_3\text{O}_4$  NPs with systematically increasing interparticle spacing were studied using the continuous and intermittent cooling protocol. The experimental evidence from dc magnetization and simulated ZFC/FC curves reveal that the increasing interparticle spacing modulated the collective magnetic behavior by effectively lowering the interparticle dipolar coupling, and for 7.5 nm  $\text{Fe}_3\text{O}_4$  NPs a noninteracting particle system formed with interparticle spacing above 31.5 nm. © 2009 American Institute of Physics. [DOI: 10.1063/1.3063032]

The intriguing properties of magnetic nanoparticles (NPs) including superparamagnetic and spin glass behavior are often ascribed to the delicate interplay between intrinsic properties and magnetostatic interactions.<sup>1,2</sup> In sufficiently dilute systems of NPs, wherein NPs are assumed to be completely separated and direct or indirect exchange coupling is neglected, the dipolar interparticle interaction has been found to play a significant role in modulating the collective magnetic behavior.<sup>3</sup> Dispersion of NPs in insert media such as  $\text{SiO}_2$ , a polymer matrix, and a liquid suspension to form a granular film or a magnetic fluid is currently used to study the dipolar interactions. This method has established several correlations between interparticle spacing and collective behavior,<sup>4,5</sup> yet some unresolved conflicts remain between experimental data and theoretical predictions. In fact, it is very difficult to avoid aggregation completely in order to obtain isolated NPs with a controlled interparticle spacing, since some magnetic clusters exist even in extremely dilute solutions.<sup>6</sup> In addition, this method cannot provide data for very high particle concentrations due to agglomeration. So there has been a great challenge: controlling the interparticle spacing, and thus dipolar interaction, for each particle even in a dense particle system. The direct manipulation of the interparticle spacing for each particle, which could further be used to vary independently each of the factors involved in determining the strength of dipolar interaction, would promote the experimental investigation of interparticle interaction based on theoretical predictions.

$\text{Fe}_3\text{O}_4$  NPs are a good candidate for studying magnetostatic interactions due to high saturation magnetization ( $M_s$ , 89 emu/g) and good chemical stability of  $\text{Fe}_3\text{O}_4$ . In this paper, we report a method to control the interparticle spacing of monodisperse  $\text{Fe}_3\text{O}_4$  NPs by the formation of a uniform non-magnetic  $\text{SiO}_2$  shell without significantly changing the magnetic properties of the  $\text{Fe}_3\text{O}_4$  core. The shell thickness, namely the interparticle spacing (the distance from center to center of NPs), can be varied from 3.0 to 20.0 nm by carefully adjusting the reaction conditions. The temperature de-

pendence of the zero-field-cooled (ZFC)/field-cooled (FC) curves and the memory effect of a suitable series of densely packed samples of NPs have been investigated in the present study.

Monodisperse 5.0–15.0 nm  $\text{Fe}_3\text{O}_4$  NPs were synthesized in octadecene, instead of the dioctyl ether used in a synthesis procedure reported by Sun and Zeng.<sup>7</sup>  $\text{SiO}_2$  coating onto the  $\text{Fe}_3\text{O}_4$  NPs was carried out in reverse micelles by the hydrolysis of tetraethyl orthosilicate.<sup>8,9</sup> Figure 1(a) shows a transmission electron microscopy (TEM) image of  $\text{Fe}_3\text{O}_4$  NPs with an average size of  $d_0=7.5$  nm. The particle size histogram was fitted using a log-normal distribution of the particle size,

$$f(d) = \frac{1}{\sqrt{2\pi}\sigma d} \exp\left(-\frac{\ln^2(d/d_0)}{2\sigma^2}\right), \quad (1)$$

where  $\sigma$  is the standard deviation. The distribution width  $\sigma=0.21$  and corresponding volume distribution  $\sigma_V=0.63(=3\sigma)$  were consequently obtained. Typical  $\text{Fe}_3\text{O}_4/\text{SiO}_2$  NPs with 3.0, 8.0, and 12.0 nm thick shells corresponding to the interparticle spacing ( $D$ ) of 13.5, 23.5, and 31.5 nm are shown in Figs. 1(b)–1(d), respectively. The size distribution of such core-shell NPs is very narrow, and every  $\text{Fe}_3\text{O}_4$  particle was coated with the  $\text{SiO}_2$  shell after the magnetic collection process. For  $\text{SiO}_2$  thickness above 8.0 nm, nearly every  $\text{Fe}_3\text{O}_4$  core was located at the center of the core-shell structures, and the  $\text{Fe}_3\text{O}_4/\text{SiO}_2$  NPs became well

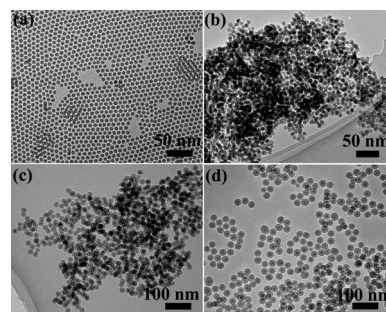


FIG. 1. TEM images of  $\text{Fe}_3\text{O}_4$  NPs with an average size of (a) 7.5 nm, the corresponding  $\text{Fe}_3\text{O}_4$ - $\text{SiO}_2$  NPs with a shell thickness of (b) 3.0, (c) 8.0, and (d) 12.0 nm, respectively.

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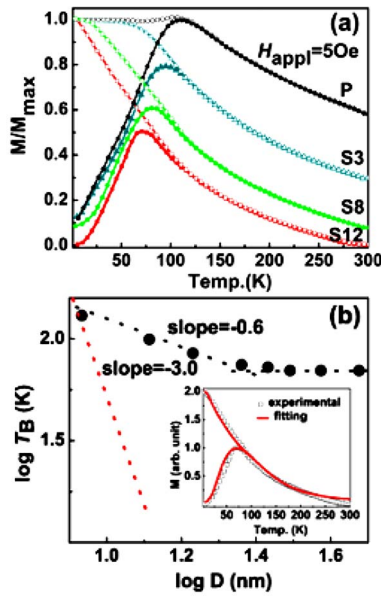


FIG. 2. (Color online) (a) ZFC (closed symbols) and FC (open symbols) magnetizations for densely packed Fe<sub>3</sub>O<sub>4</sub> NPs powder (P) and Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub> NPs with an interparticle spacing of 13.5 (S3), 23.5 (S8), and 31.5 (S12) nm, respectively. (b) The variation in the blocking temperature with the interparticle spacing for 7.5 nm Fe<sub>3</sub>O<sub>4</sub> NPs. The red dashed line is the theoretical prediction of an inverse cubic relationship between  $T_B$  and interparticle spacing. The inset is the fit (solid line) to Eqs. (2) and (3) using the log-normal size distribution.

dispersed in ethanol, which provide an indirect evidence of the decrease in interparticle interaction. Moreover, compared to the as-prepared Fe<sub>3</sub>O<sub>4</sub> NPs, the  $M_s$  of the Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub> NPs showed a decrease of less than 1.5% even though Fe<sub>3</sub>O<sub>4</sub> NPs were immersed in ammonia to form a SiO<sub>2</sub> shell.

To determine the effect of interparticle spacing on the collective magnetic behavior of the Fe<sub>3</sub>O<sub>4</sub> NPs, the temperature-dependent ZFC/FC magnetization of the as-prepared 7.5 nm Fe<sub>3</sub>O<sub>4</sub>(P) and Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub> NPs with different interparticle spacings of 13.5(S3), 23.5(S8), and 31.5(S12) nm is shown in Fig. 2(a), measured at low magnetic fields (5 Oe) to avoid nonlinear effects. With increasing interparticle spacing, the maxima of the ZFC curves related to the mean blocking temperatures ( $T_B$ ), as well as the splitting points ( $T_{irr}$ ) between the ZFC and FC curves, shift toward lower temperatures.  $T_B$  decreased from 110 to 70 K as the interparticle spacing increased to 31.5 nm. A similar trend was previously observed in dilute dispersed magnetic NPs and in Monte Carlo simulations.<sup>10</sup> A more remarkable effect of the dipolar interaction can be seen in the FC magnetization curvature in the irreversibility region ( $T < T_{irr}$ ), qualitatively indicating the strength of the interparticle interaction, diminishing its relative height with respect to the maximum of the ZFC curve as the shell thickness decreased. For sample P, the ZFC/FC curves bifurcate at a temperature very close to the peak position of the ZFC. The FC curve does not increase but stays almost constant below  $T_B$ , which is the primary indicator for the superspin glassy state. On the other hand, the ZFC/FC curves for sample S12 bifurcate at a temperature away from the peak position of the ZFC curve and the FC magnetization curvature rises almost linearly toward low temperature. For sample S3 and S8, the bifurcation is close to the peak position of the ZFC curve and the FC magnetization curvature rises smoothly. It is worth mention-

ing that the overall shape of all ZFC curves is similar, indicating that no percolation occurred among the NPs even in the absence of a shell. This is possibly because surfactants with an  $\sim 2$  nm chain length form a tight coating layer and prevent the NPs from contacting.

The blocking temperature as a function of interparticle spacing is shown in Fig. 2(b). Closer analysis suggests that  $T_B$  follows a  $T_B \sim (D/d)^{0.6}$  dependence for interparticle spacing below 27.5 nm and remains constant above this value. This trend suggests that NPs with spacing beyond a certain interparticle spacing act seemingly independent of one another. This observation is in stark contrast to earlier dilution studies wherein the statistical distribution, typically using a volume fraction less than 0.1 vol % in terms of interparticle spacing more than 80 nm, was required to eliminate particle interaction orders of magnitude larger than reported here.<sup>11,12</sup> The key difference is our use of SiO<sub>2</sub> to specifically control the interparticle spacing of every particle, allowing us to take advantage of the dramatic dependence of collective behavior on interparticle spacing and create densely packed samples with negligible interparticle interactions. It should be noted that our experimental data do not support a recent set of calculations that indicate that  $T_B$  of NPs interacting through dipolar coupling should follow an inverse cubic dependence on interparticle spacing.<sup>13</sup> Based on these results, the Fe<sub>3</sub>O<sub>4</sub> NPs without the SiO<sub>2</sub> coating can be referred to as a strong interacting particle system, those with a 13.5–27.5 nm interparticle spacing as a weak interacting particle system, and those with an interparticle spacing of above 31.5 nm as a noninteracting particle system.

Consequently, the magnetic properties of Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub> NPs with interparticle spacing of above 31.5 nm can be described within the framework of the superparamagnetic model. For a single particle of volume  $V$ , the magnetization  $M$  under a low magnetic field  $H$  is expressed as  $M = (M_s)^2 VH/k_B T$  in the superparamagnetic region ( $T > T_B$ ), and  $M = (M_s)^2 H/3K$  in the blocked region ( $T < T_B$ ), respectively.<sup>14</sup> Therefore, for a noninteracting particle system, the total magnetization can be written as<sup>15</sup>

$$M_{ZFC}(H, T) = \frac{M_s^2 H}{3k_B T} \int_0^{V_b(T)} V f(V) dV + \frac{M_s^2 H}{3K} \int_{V_b(T)}^{\infty} f(V) dV, \quad (2)$$

$$M_{FC}(H, T) = \frac{M_s^2 H V_b(T)}{3k_B T} \int_0^{V_b(T)} f(V) dV + \frac{M_s^2 H \ln\left(\frac{t_m}{\tau_0}\right)}{3K} \int_{V_b(T)}^{\infty} f(V) dV, \quad (3)$$

where  $f(V)$  is the particle volume distribution as described in  $f(d)$ . Using the model for ZFC/FC curves for noninteracting NPs, we have fitted the experimental curves to Eqs. (2) and (3). The result for the ZFC/FC curves is shown as a solid line in the inset of Fig. 2(b). Note that these fits do not exactly match the experimental data; however, there is only a slight difference between the experimental and expected values of  $T_B$ , 70.0 and 69.2 K, possibly due to the interface effects with the SiO<sub>2</sub> shell. This strongly suggests that an interparticle spacing of 31.5 nm is sufficient to achieve an exact noninteracting particle system for the 7.5 nm Fe<sub>3</sub>O<sub>4</sub> NPs.



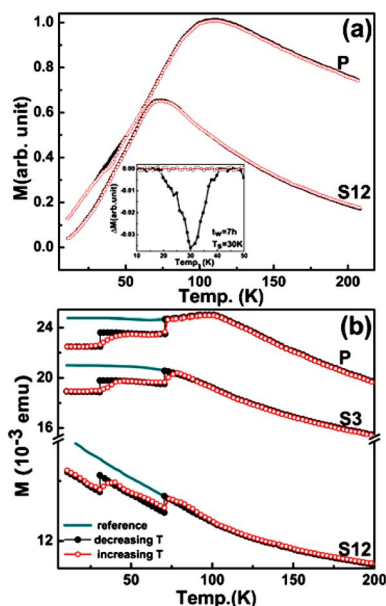


FIG. 3. (Color online) (a) Temperature-dependent ZFC magnetizations for densely packed  $\text{Fe}_3\text{O}_4$  NPs powder and  $\text{Fe}_3\text{O}_4/\text{SiO}_2$  NPs with an interparticle spacing of 31.5 nm using normal cooling protocol and an intermittent stop at 30 K for 7 h; the inset shows the difference ( $\Delta M$ ) with the corresponding reference. (b) The temperature-dependent FC magnetization of  $\text{Fe}_3\text{O}_4$  NPs powder and  $\text{Fe}_3\text{O}_4/\text{SiO}_2$  NPs with an interparticle spacing of 13.5 and 31.5 nm during cooling with intermittent stop at 70 and 30 K (open symbols) and the subsequent reheating (solid symbols).

To gain further insight into the influence of interparticle spacing on the collective magnetic properties of NPs, the history-dependent behavior of the resultant  $\text{Fe}_3\text{O}_4/\text{SiO}_2$  NPs was also investigated to delineate the extent of the spin-glass-like character. Since a memory effect of ZFC magnetization with an intermittent stop during cooling can be observed in spin glass and interacting particle systems, not in noninteracting particle systems, the ZFC protocol suggested by Mathieu *et al.*<sup>16</sup> is used to confirm the formation of a noninteracting system for 7.5 nm  $\text{Fe}_3\text{O}_4$  NPs with a 31.5 nm interparticle spacing.<sup>17</sup> The normal ZFC without any stop during cooling is also recorded as a reference curve. Figure 3(a) shows the results for sample P and S12. For the latter, the curve with a stop and the reference curve almost completely overlap. However, for the sample P a memory dip shows up in the vicinity of 30 K upon reheating. In order to clearly show the difference between the aged and normal ZFC magnetization, we plot the difference in magnetization,  $\Delta M = M(T) - M_{\text{ref}}(T)$ , in the inset of Fig. 3(a). The absence of a memory effect of magnetization further supports our supposition that sample S12 is a noninteracting particle system. Moreover, the memory effect of the FC magnetization is obtained from a similar protocol, except for the fact that the sample is cooled in a 100 Oe field and the field is cut off during intermittent stops of the cooling at  $T = 70$  and 30 K for 1 h at each stop. For all three samples, a striking result is that the system clearly remembers its thermal history as the curve reproduces the steplike shapes and the warming  $M(T)$  curve recovers the cooling one within 2–4 K in the vicinity of the temperatures of 30 and 70 K [shown as open circles in Fig. 3(b)]. Thus, this noninteracting particle system exhibits a strikingly strong similarity to the memory behavior observed in the strong interacting system. The spin-glass-like dynamics, such as the memory effect and aging phenomena, have

been observed both in the particle systems with a strong and no dipolar interaction.<sup>18,19</sup> However, since magnetic clusters are unavoidably formed even in extremely dilute particle systems, there is always the absence of strong evidence to suggest that the memory effect originates from a distribution of energy barriers in noninteracting particle systems with a size distribution, wherein the results are consistent with the simple thermal activation model. Here, our experimental data from an exact noninteracting system reveal a strong evidence to support such an argument.

In conclusion, we have shown that  $\text{SiO}_2$ -mediated interparticle spacing effectively modulates the collective behavior of magnetic NPs. The dependence of the blocking temperature on interparticle spacing was found to deviate from a recent theoretical model and point toward strong interdependence at close interparticle spacing and a weak correlation for larger spacings. Based on the dc magnetization experiments, we found that a relatively modest increase in interparticle spacing was sufficient to suggest fully independent NPs within a densely packed sample, not like in a dilute particle solution. We are currently undertaking a more rigorous set of experiments, including the thermal variation in the ac susceptibility of different frequencies and the critical interparticle spacing of different sizes and  $M_s$  of NPs for a noninteracting system, coupled to micromagnetic modeling to further evaluate the interparticle interaction strength and understand the intricate macroscopic magnetic behavior of a superparamagnetic system with a dipolar interaction.

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