Dynamic spin freezing in magnetic ensembles of interacting anisotropic nanoparticles

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We explore the influence of demagnetizing interaction on dynamic magnetic response of two different ensembles of anisotropic nanoparticles with varying geometry organization. The ensemble having hollow interior shows enhanced magnetic memory effect with lower blocking temperature and higher coercivity over the compact ensemble. It is due to the combined effects of higher demagnetizing interaction and enhanced magnetic anisotropy generated due to hollow geometry which adds higher degree of frustration on the surface spins. The progressive spin freezing on experimental time period is reflected in both the ensembles with complex landscape of anisotropic energy.

Self-assembled nanoscaled magnetic nanoparticles are usually influenced by effect of interparticle interaction, as energy barriers of magnetic anisotropy plays crucial role to define collective magnetic behaviors [1, 2]. For single domain magnetic nanoparticle, time dependent magnetization can be explained with regard to thermally activated relaxation for two different magnetization states, segregated by explicit energy barrier [3]. In such case, individual magnetic moments can be considered as super-spins [4], which can flip randomly. In absence of interaction among super-spins, magnetic behaviors are dominated by superparamagnetic relaxation [5]. The fluctuation among their magnetic easy axis occurs resulting freezing of super-spins at blocking temperature along their preferred direction [6]. When these single domain nanoparticles are congregated, dynamic behavior begins to be utterly dependent on respective strength of interparticle interaction and anisotropy energy [7]. With gradual enhancement in dipolar strength, spin dynamics signalized by effective duration are extended, which can further classify the behavior of nanoparticles [8-12]. The impact of demagnetizing interaction on moment relaxation is explained by Dormann-Bessais-Fiorani (DBF) model [13] and Shtrikman-Wohlfarth model [14] which predict slowing of moment relaxation period with enhancement in dipolar-interaction. In contrast, Morup and Tronc (MT) model [15] predicts faster relaxation with increasing dipolar interaction. These contradictory hypotheses provide ambiguity regarding interparticle interaction in nanoparticle assembly. With increase in demagnetizing strength yielding from magnetic interaction, a crossover from blocking of individual particle to freezing of collective moments of particles occurs resulting super-spin glass state [12]. When interaction become very strong, collective spin freezing occurs because of disordered and frustrated spins at low temperature. This phenomenon differs for a system having disordered spin in surface where energy barriers are distributed irregularly with complex landscape [10]. Thus, surface spin having multiple degree of freedom are compelled toward spin glass state due to freezing of spins at low temperature [12, 15]. Moreover, spin freezing is found due to surface spin disorderness in isotropic maghemite nanoparticles having hollow core which is evaluated by Monte-Carlo simulation [19]. Many isotropic ferrite nanoparticles are manifested where glassy behavior is credited to super-spin glassy state along with randomly oriented surface spin freezing [21]. All these studies consider random distribution of spins and ensemble of isotropic nanoparticles, but not particular geometry of the ensemble. But present study is the first investigation of its kind regarding spin glass freezing of ensemble of anisotropic nanoparticles with varied organization pattern.

In this letter, we investigate collective magnetic response in three dimensional ensemble of anisotropic \( \text{ZnFe}_2\text{O}_4 \) nanoparticles with optimized inter-particle space by considering role of demagnetizing interaction among spins by developing two different systems: (a) Compact ensemble (CE), (b) Hollow core ensemble (HCE). We evaluate the static and dynamic magnetic behavior by considering the geometry of the ensembles and alignment of disordered spins along with demagnetization interaction. Moreover, presence of a hollow core in an ensemble will enhance the surface driven effects, which will be reinforced by enhanced surface area and modified anisotropy along with thermal memory effect in comparison to similar solid assembly.

To develop CE and HCE, we employ template free Solvothermal technique (Synthesis and Characterization techniques is given in the Supplemental Material [22]). We perform High Resolution Transmission Electron Microscopy (HRTEM) analysis to ensure formation of spherical ensemble of anisotropic nanoparticles (Fig 1 (a-f); Fig. S3, S4, S5 [22]). CE is obtained from 12 hours reaction time where anisotropic nanoparticles having average size 5±2 nm are assembled with some inter-particle space. We increase the reaction time to 21 hours to obtain ensemble containing hollow core. An increase in reaction period leads to lower in crystal defects and larger hollow ensemble with larger domain size result-

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ing better crystallinity. Selected Area Electron Diffraction (SAED) pattern, FFT, inter-planar distance, Energy dispersive X-ray (EDX) and X-ray diffraction (XRD) show the crystallographic evident of cubic spinel phase of ZnFe₂O₄ (Fig. S6, S7, S8, S9, S10, S11 [22]). Fig. 1 (g, h) show the Small Angle X-ray Scattering (SAXS) and Small Angle Neutron Scattering (SANS) plots (fitting details, Fig. S12, S13 [22]) which are supporting the presence of two types of hierarchy corroborating the HRTEM results. The scattering data ensures the presence of sticky hard sphere type interaction along with packing fraction (φ) 0.20 and 0.32 for CE and HCE respectively.

In order to further verify magnetic behavior, we study dc magnetization extensively. Field dependent magnetization (M-H) are shown in Fig. 2(a, d) with variation in temperature. The narrow hysteresis nature indicates presence of superparamagnetic state [5] (Table S3, [22]) [24]. Using Zero-Field Cooling (ZFC) and Field Cooling (FC) conditions, temperature dependent magnetization plots are executed with the presence of single domain nanoparticles with uniaxial anisotropy (Table S1, [22]) [25]. Blocking temperature (T_B) signifies the thermal energy required to cross over energy barrier of super-exchange transition. Blocking temperature shifts toward lower temperature for HCE. Here, magnetization saturate below blocking temperature which indicates presence of strong interaction among the grains in ensembles [1]. When system is being cooled, magnetic moments start to align partially in the direction of applied field. During warming, increase in thermal fluctuation results decrease in magnetic moments along field projection. Here, primary nanoparticles are firmly packed resulting formation of coupling of magnetic moments. This facilitates magnetic moment ordering and consequently opposes impact of thermal fluctuation. To reveal the essence of interaction, we analyzed the remanence curves which depend on rotation of irreversible magnetization. It provides evidence related to interaction by use of Henkel plots [8] which is obtained from Direct Current Demagnetization (DCD) as well as Isothermal Remanent Magnetization (IRM) curves (Protocols for IRM/DCD measurement [22]). For single domain-non-interacting system with uniaxial anisotropy, IRM and DCD are correlated using Wohlfarth expression:

\[
m^{DCD}(H) = 1 - m^{IRM}(H),
\]

where, \(m^{DCD}(H)\) and \(m^{IRM}\) stand for reduced remanence magnetization of DCD and IRM respectively. This results a straight line for non-interacting system. In contrast if the system is interacting in nature, deviation of Henkel plot from linearity is observed. To determine the deviation, \(\delta M\) can be defined as,

\[
\delta M = m^{DCD}(H) - [1 - 2m^{IRM}(H)].
\]

The observed negative deviation of \(\delta M\) (Fig. 2(g, h)) reveal that dipolar type of interaction is dominating among nanoparticles with uniaxial anisotropy [26]. HCE is showing higher interaction over system CE. Though HCE is having hollow interior, nanoparticles are highly compact in surface resulting enhancement in net dipolar strength. In addition, differentiation of normalized DCD and IRM curves are plotted to analyze distribution of energy barrier. Considering both the remanence curves, irreversible susceptibility can be compared as,

\[
\frac{\partial m^{DCD}}{\partial H} = 2 \frac{\partial m^{IRM}}{\partial H}. \]

The magnitude of interaction field \(H_{int}\) can be expressed as follows,

\[
H_{int} = \frac{1}{2}(H_r - H^*),
\]

where, \(H_r\) and \(H^*\) refers to peak position of field derivative of moments for IRM and DCD respectively. The calculated values of \(H_{int}\) are found as -0.25 kOe and -0.45 kOe.
for CE and HCE respectively (Table S4 [22]). The negative value indicates pre-domination of demagnetization effect corroborating negative deviation observed in δM plots. The higher magnitude of $H_{\text{int}}$ for HCE ensures higher demagnetization effect than CE.

Though HCE has higher demagnetization effect, coercivity value is higher in HCE (37.8 emu/g) over CE (10.6 emu/g), which is showing an unusual trend. Conventionally, strong demagnetizing effect helps in making magnetic reversal act easy. But here, enhanced dipolar interaction helps for enhancement in coercivity [27]. In essence, strong demagnetization strength leads to intense energy barriers in complex interacting energy landscape. It results attractive configurations being more strongly attractive. The required thermal energy to overcome these complex landscape energy barrier needs to be enhanced. If thermal energy was not sufficient enough, it would be less probable to overcome energy barriers resulting enhancement of coercivity. In addition, value of reduced remanence can be analysed from consequence of competition arises between interparticle anisotropy and dominant demagnetizing interaction on the process of spin relaxation which results frustration. The dependence of blocking temperature on strength of interaction is also showing an unusual trend as it is shifting towards lower temperature value with stronger demagnetization strength, which is not consistent with DBF model. This may be due to rapid spin relaxation compelled by higher demagnetization effect. In addition to higher interaction, the hollow geometry of the ensemble include extra surface driven parameters for modulation of the magnetic nature. The presence of hollow interior provide enhanced surface effects like large surface to volume ratio with lowest energy domains configuration. Moreover, the broken symmetry of the surface with low coordination provides higher magnetic anisotropy.

We perform Field-Cooling (FC) memory effect below blocking temperature to clarify influence of geometry organization of the spins in dynamic magnetic property (protocol is supported in the Supplemental Material [22]). CE able to memorize two pronounced steps at 20 K and at 80 K left throughout the cooling process. Moreover, HCE is manifesting distinctly four steps of memory (Fig. 3(a-d)). The observed steps ensure that system retrieve energy configuration which is marked by energy barrier redistribution through cooling process. CE having lower interparticle interaction could recover only lower energy magnetic arrangement. The increasing trend of moments in cooling curve up to 30 K for CE and up to 80 K for HCE manifest the super spin glass (SSG) state bellow 30 K and 80 K respectively. Moreover, FC memory effect is a signature of both superparamagnetic and spin glass system, one cannot give conclusive statement in this regard. To further differentiate among these two states, ZFC memory effect and relaxation dynamics are evaluated which are the hallmarks of spin glassy phase.

A spin glass system exhibits non-equilibrium nature as
ference curve (Fig. 4(a, b)) shows a prominent dip in case of both the systems. It provides evidence of spin glassy state in systems as moment dynamics has slowed down below a certain temperature. The observed non zero moment $\Delta M$ in between temperature range 10 K to 50 K for CE and 10 K to 100 K for HCE ensure that systems get relaxed towards steady dynamics during foisted waiting time, as explained in both spin glass models, hierarchical energy model and spin droplet model [28, 29]. In spin droplet case, excitation of spin glass configure compact domains and non-equilibrium behaviour of spin dynamics increases volume of droplet with time. During aging, as temperature becomes constant, growth of droplet and frozen energy barrier associated with it occurs simultaneously due to absence of perturbation. It can be recovered once warming starts. At stopping temperature, adequately low energy barriers results in flipping of thermally energetic cluster upon warming and provides low magnetization moments during memory path $M_{mem,ZFC}$ over reference curve $M_{ref,ZFC}$. The combine effect of interparticle interaction and the disordered spin of the ensembles provide high degree of frustration to the systems. The randomly distributed primary nanoparticles along with their randomly directed anisotropy axes lead to frustration in spins resulting super spin glass (SSG) state. The anisotropic nanoparticles of system CE bearing uniaxial anisotropy are arranged in such a way that there is an optimum interparticle space among them resulting less dipolar strength with lower magnetic anisotropy. The presence of space among each particles allow rotation of individual spin and results less complex energy landscape. Due to which, slow spin dynamics is observed only at narrow $\Delta M$ range. On contrast, spins of anisotropic nanoparticles present in surface of HCE are having higher degree of frustration due to existence of strong interparticle interaction. Presence of strongly disordered surface layers in the hollow ensemble makes the system highly complex energy landscape with enhanced magnetic anisotropy, which results wider $\Delta M$ range. It is evident from anisotropy constant calculation that HCE is showing higher value over CE. The higher anisotropy constant provides wider range of $\Delta M$ because, enhancement in surface anisotropy occurs due to highly disorderness in surface spins along with the contribution of hollow geometry of the ensemble, and aging effect strongly depends on surface anisotropy [30].

We further examine magnetic relaxation study using ZFC protocol in both the systems. The systems are cooled to temperature 30 K ($T_1$) and aged for a period of 5000 seconds ($t_1$) at applied field 50 Oe. Aging can be observed as a significance of jagged nature of disordered landscape of spins. This conforms to the crossing of thermally activated energy barriers leading to slow relaxation of the spins towards minimum energy levels [31]. As the moments unable to attain its equilibrium state, they start to relax very slowly towards the direction of the applied field and follows a logarithmic trend as shown in Fig. 4 (c, d) marked as aging. Further, the systems were temporary cooled down to 20 K ($T_2$) and the moment was measured for the period of 7000 seconds ($t_2$). At this step the spin dynamics is not following the trend of $T_1$, but the moments are arrested and become constant during this entire period. The frozen spins start to adjust at $T_2$ and refuse to slow down with free energy barriers. When temperature comes to $T_1$, moments recommence its ascending relaxation trend from preceding value. The systems able to memorize strongly its age at $T_1$. The continuity of moment relaxation observes in joined curves for $T_1$ and $T_2$ (Fig. 4(e, f)) signifying the memory effect and complete freezing dynamics between 20 K and 30 K in both the systems. The non-compact spin clusters are large enough and it cannot be frozen at high temperature but left the surrounding spins comparatively free. As temperature starts to increase, small small cluster of spins begin to freeze resulting an aging signal, whereas large spin cluster begin to be blocked completely resulting memory effect. The interparticle interaction plays a dominant role to produce hierarchical organization of the complex free energy landscape as hierarchical arrangement needs higher number of degree of freedom to be integrated which is not possible in case of independent particles. Thus, the presence of memory features is a consequence of frustration arising due to the competition between disordered spins and crystallographic anisotropy which depends not only on the shape, size, compactness and interparticle interaction of the nanoparticles, but also the relative geometry organization of the magnetic ensembles.

![Fig. 4. ZFC memory effect](image-url)
In summary, we develop two differently organized systems CE and HCE by tuning interparticle spacing and investigate extensively their dynamic magnetic nature. Both the ensembles are exhibiting slow spin dynamics and aging nature at low temperature. Both FC/ZFC memory effect and spin relaxation experiments evident presence of spin glass state with establishment of spin frozen state below 20K. Moreover, HCE having higher demagnetization strength is exhibiting all prominent FC memory and wider non-zero range of $\Delta M$ (upto 100 K) in ZFC memory effect which is due to its highly disordered and frustrated surface spins in addition to its hollow core which enhance the surface driven effects. An unusual behaviour is observed in the trend of coercivity with enhanced demagnetization interaction which can be correlated with enhancement in random distribution of anisotropy energy barrier due to complex interacting energy landscape. Interestingly, decrease in blocking temperature trend in HCE is because of quick spin relaxation due to increase in frustration of spins arising from higher interaction. Therefore, we demonstrate a way to regulate coercivity, magnetic anisotropy and spin relaxation dynamics by simply tuning the distribution of spins and geometry of ensemble which will unbolt new potential application as “Thermal Memory Cell” based on their unique magnetic behaviour.

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