Dynamic magnetic responses and quantum phenomena in magnetic ensembles of interacting nanosystems

Abstract

Nanomagnets exhibit extraordinary significance in an extensive array of scientific disciplines because of their intriguing innate behaviours. Fundamental studies of such magnetic nanosystems, along with their technical applicability in a variety of domains, have generated a lot of interest [1-4]. When size reduces to a specific critical dimension, efficiency of such particles is found to be at its peak. The nanoparticle in 10-20 nm range is in typical single-domain limit, having superparamagnetic behaviour below a certain temperature addressed as blocking temperature [5]. Such single-domain nanoparticles act like giant paramagnetic atoms with minimal remanence and coercivity, exhibiting a quick response to external magnetic field.

In an ensemble of such single domain nanosystems, if the individual nanosystems maintain an apparent separation, the superparamagnetic characteristics persist. Reduction in interparticle separation enables numerous kinds of interactions amongst the primary nanosystems, which subsequently result in collective magnetic nature [6, 7]. In this scenario, the mere existence of interaction causes energy barrier regulations. The energy barriers are also impacted by the direct alteration of a single primary nanosystem in such ensembles [8]. The volume of the nanoparticles in their ensemble affects the degree of interaction strength. Further, interparticle interaction dominates the blocking of individual nanosystems, which subsequently leads to a collective freezing of spins [9, 10]. The shape/size distribution of nanoparticles induce magnetic moment variation, which leads to complexity in their inherent magnetic behaviour [11]. The impact of interaction in an ensemble of interacting nanoparticles can be comprehended by monitoring numerous low-temperature phase transitions such as the super-spin glass (SSG) phase [12], the super-ferromagnetic phase [13], etc. Such ensembles of interacting nanoparticles with fascinating dynamic magnetic responses exhibit various quantum phenomena

and spin relaxation dependence on interaction strength [14. 15]. However, the interaction dependence with moment relaxation is needed to be explored by considering the easy axes alignment and simultaneous anisotropy energy complexity in such complex ensembles, which might have a substantial impact on energy barrier modulations.

The focus of the thesis is based on the spin dynamics behaviour of ensembles of various isotropic/anisotropic magnetic nanosystems such as: nanorods, spherical nanoparticles, two-dimensional flakes, bi-magnetic and tri-magnetic ensembles, and a disintegrated framework. The alignment of easy axes and complexity of anisotropy landscape are considered. The collective magnetic properties with non-ergodic behaviour are considered with the aid of various geometric organization of ensembles. Further, structure-relaxivity correlation is addressed by considering another quantum phenomenon known as Magnetic Resonance (MR)-relaxivity in various ensembles of isotropic and anisotropic nanosystems. The chapterization is given as follows:

Chapter 1: This chapter provides a prologue about ensembles of interacting nanosystems and their interaction-dependent modification of inherent magnetic behaviours. The present scenario of the research field, with prior literature, and motivation are also presented.

Chapter 2: This chapter presents the dynamic magnetic responses of various geometric organized ensembles comprised of Zinc Ferrite nanorods. A strategy that considered for influence of geometrical arrangement of MNPs and easy axes distribution addresses the dependence of interparticle interaction on moment relaxation. Magnetic anisotropy energy and spin frustration can be tuned with changing interacting strength between aligned domains and respective organisation geometry. Additionally, it has been demonstrated that the demagnetizing field's influence on moment relaxation. As a consequence, the resulting rise of magnetic memory effects correlates with their influence on the change of anisotropic energy landscape.

Chapter 3: This chapter provides a detailed spin-dynamics behaviour of an ensemble comprised of two-dimensional flakes of manganese dioxide decorated over nickel ferrite nanoparticles (δ-MnO_2@$NiFe_2O_4$) named Ensemble of Two-Dimensional flakes (ETD). The correlation of low-temperature slower spin relaxation with high magneto-crystalline anisotropy, robust bonding, and high exchange field strength is represented in this ensemble with fascinating magnetic behaviour. Interestingly, prominent magnetic memory effects in Field Cooling (FC)/Zero Field Cooling (ZFC) conditions with significant ageing relaxation are achieved, which is triggered by the evolution of cluster spin-glass state with complex energy landscape.

Chapter 4: This chapter yields dynamic magnetic responses of the disassembled form of manganese dioxide over nickel ferrite nanoparticles (α-MnO_2@$NiFe_2O_4$) named Disassembled Anisotropic Nanosystem (DAN). The interacting superparamagnetic state with magneto-crystalline anisotropy and exchange field strength is correlated with enchanting magnetic behaviour. Both FC and ZFC magnetic memory effects are achieved because of interacting superparamagnetic domains. However, the asymmetric ageing relaxation trend is a reflection of the non-dominance of spin freezing in the disassembled framework.

Chapter 5: This chapter represents the magnetic relaxivity analyses of ensembles of isotropic nanoparticles by considering water proton dephasing in MRI study. MR-transverse relaxivity is revealed by considering two different ensembles, $Ni_{1-x}Zn_xFe_2O_4$@CoO (x=0.25, 0.50). The collective magnetic behaviour is depicted systematically. Shifting of room temperature blocking towards lower temperature with higher magneto-crystalline anisotropy appears with an increase in octahedral site substitution. A correlation of anisotropy energy, alignment of competing moments with enhancement in MR-relaxivity is drawn.

Chapter 6: This chapter explores the relationship between structure and MR-relaxivity by comparing widely arranged superparamagnetic complex ensembles of zinc ferrite nanorods while also highlighting transverse relaxivity improvement in MRI. The investigated superparamagnetic systems exhibit easy axes alignment, highly anisotropic energy landscape, and a relationship between MRI-transverse relaxivity, and spatial organisation of MNPs. Modulation in MR-relaxation is triggered by the coexistence of alignment in aligned easy axes and an elevated anisotropy constant. As a result, the hollow core ensemble of anisotropic nanosystems achieves better contrast efficiency.

Chapter 7: This chapter discuss an approach for obtaining MR-transverse relaxivity by taking into account a bi-magnetic competitive ensemble of cluster spin-glass (CSG) hybrid system composed of Zinc Ferrite nanorods' ensemble along with maghemite nanoparticles, γ-Fe_2O_3@$ZnFe_2O_4$. In order to validate the existence of interacting domains with CSG state, dynamic magnetic studies are carried out. The competing spin dynamics causes frustrated magnetic state, which in turn causes an inhomogeneous magnetic field and a complicated anisotropy energy landscape. This accelerates the decay of water protons and increases MR-transverse relaxivity and signal strength. The promising cell-viable system gives higher r_2/r_1 having enhanced MR-relaxivity, with a 1.4 T magnetic field and up to a low metal concentration, 0.1 mM.

Chapter 8: This chapter represents a competing isotropic-anisotropic tri-magnetic hybrid nanosystem, γ-Fe_2O_3@δ-MnO_2@$NiFe_2O_4$, for MR-transverse relaxivity investigation. An interesting dynamic magnetic behaviour is revealed by the interacting superparamagnetic system, where two-dimensional flakes adorned with MNPs. Improvement in MR-transverse relaxivity is rendered by controlled shape anisotropy, spin blocking, as well as energy barrier broadening. Superior MR-transverse relaxivity is displayed by the hierarchical architecture of hybrid ensemble. It has been found that the system with controlled activation energy is what causes the signal amplification in MR-transverse relaxivity.

Chapter 9: This chapter provides a summary of conclusions drawn from each of the preceding chapters regarding dynamic magnetic responses in ensembles of various nanosystems and the underlying mechanism for the robust Magnetic Resonance Relaxivity in the developed interacting ensembles. This chapter also focuses on potential implications of the research represented in the thesis.

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