DYNAMIC MAGNETIC RESPONSES AND QUANTUM PHENOMENA IN MAGNETIC ENSEMBLES OF INTERACTING NANOSYSTEMS

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Chapter 9

Concluding remarks and Future direction

9.1 Thesis Conclusion

The major findings of the thesis are depicted below:

- The present thesis work addresses the impact of dynamic spin relaxation on demagnetizing interactions by considering an ensemble of interacting anisotropic nanosystems. Two differently organized ensembles of interacting anisotropic $ZnFe_2O_4$ nanorods: a Compact Ensemble (CEZF) and a Hollow Core Ensemble (HCEZF) are considered to explore the dynamic magnetic responses. Numerous intermediate metastable states and considerable memory effects support the gradual spin freezing. A complicated anisotropic energy landscape results from the coexistence of hollow core geometry, strongly interacted surface MNPs, and partial alignment in easy axes. In comparison to CEZF, HCEZF exhibits an enhanced magnetic memory effect combined with higher activation energy, lower blocking temperature, and improved coercivity. The degree of alignment in magnetic easy axes and magneto-crystalline anisotropy are found to be important factors in overcoming the spin relaxation anomaly in interacting ensembles.
- The underlying mechanism of ergodicity with a prominent magnetic memory effect is found to be governed by the degree of freedom in metastable states and competition between dipolar and exchange field interaction along with spin frustration. The non-ergodic dynamics in cluster spin-glass ensembles of frustrated two-dimensional nanoflakes with nanoparticles with emerging magnetic memory effects are explored by considering δ-MnO_2@$NiFe_2O_4$. Such competing magnetic frustration is due to the presence of sufficiently

high magneto-crystalline anisotropy with a strong random anisotropy field and strong exchange field. However, when the reaction period is increased, the ensemble of two-dimensional flakes is disintegrated with a phase transition and an interacting superparamagnetic system, α-MnO_2@$NiFe_2O_4$ with prominent magnetic memory effects is achieved with asymmetric ageing relaxation trend. However, α-MnO_2@$NiFe_2O_4$ shows prominent Field Cooling magnetic memory effects with Zero Field Cooling magnetic memory effects, as a result of interacting superparamagnetic domains. The hierarchical organization of metastable states is dominating the cluster SG system with prominent memory effect, negative T-cycle based ageing memory imprint, and asymmetric nature in reverse ageing relaxation trend in δ-MnO_2@$NiFe_2O_4$, compared to α-MnO_2@$NiFe_2O_4$ with interacting superparamagnetic state. The interplay of significant exchange coupling in interfacial spins and dipolar interaction is the underlying reason for such quantum non-ergodic phenomena. Accordingly, cluster spin glassy state with enhanced anisotropy landscape and robust bonding shows significant ageing relaxation compared to interacting superparamagnetic state.

- In order to maximise the potency of Magnetic Resonance Imaging (MRI) contrast, an ensemble of magnetic nanosystems is believed to be a practical method for producing effectual transverse (r_2) or longitudinal relaxivity (r_1). An appealing strategy is to take into consideration an ensemble of highly concentrated interacting magnetic nanoparticles (MNPs) to seek modulation of longitudinal and transverse MR-relaxivity and achieving a productive real-time application. In accordance with quantum-mechanical Outer-Sphere theory, the characterizations including shape/size, water penetration nature, the composition of the nanosystem, etc. could affect the MR-relaxivity. Employing an ensemble of magnetic superparamagnetic nanoparticles is an intriguing strategy for achieving effective transverse (r_2) MR-relaxivity, and superparamagnetic properties are desirable for MR imaging for real-time applications. In addition, the transverse relaxivity of superparamagnetic NPs

can only be laid out by the quantum-mechanical outer-sphere theory until it reaches a size threshold satisfying the MAR (outer-sphere motional averaging regime) criterion. In accordance with MAR, transverse relaxivity is related to water proton diffusion and the fundamental physical characteristics of MNPs, which can be adjusted by modifying microstructural features and surface-induced characteristics, including proton dephasing in individual MNPs domain. While the size of nanoparticles exceeds the ideal MAR threshold limit, the static dephasing regime (SDR) and echo-limiting regime ought to be addressed to comprehend transverse relaxivity. Proton dephasing in transverse relaxivity deriving from an inhomogeneous anisotropy landscape is an unsolved problem, as saturation magnetization independently is unable to clarify the fundamental principle of MR-relaxivity. The inhomogeneous anisotropy triggered by the exchange field is found to be responsible for achieving enhanced MR- transverse relaxivity while considering nano-ensembles of isotropic $Ni_{1-x}Zn_xFe_2O_4$@CoO (x=0.25, 0.50) nanoparticles. A correlation of MR-transverse relaxivity enhancement is achieved with anisotropy energy, magnetic moment alignment, and competitive interactions among the moments in an interacting superparamagnetic system. The octahedral site replacement provides tailored magnetic linkage having ground state magnetizations of 210.6 μ_B/cell for $Ni_{0.75}Zn_{0.25}Fe_2O_4$@CoO and 207.1 μ_B/cell for $Ni_{0.5}Zn_{0.5}Fe_2O_4$@CoO. $Ni_{0.75}Zn_{0.25}Fe_2O_4$@Co demonstrates an enhanced asymmetric coercive field and exchange field through a broad distribution of easy axes across the anisotropic energy landscape, resulting in a raised MR-transverse relaxation. The distinct insights surmount the inadequacy of existing classical and quantum outer sphere model for deciphering transverse effects for potent MRI-contrast applications.

- The structure-dependent transverse/spin-spin relaxivity by realising the spatial arrangement of primary nanoparticles, the relative position of easy axes, and the anisotropy energy landscape are assessed. The ensemble of spherical nanoparticles possesses randomly oriented easy axes and a greater

value of anisotropy constant, resulting in improved T_2 transverse contrast efficacy. Yet, an ensemble of isotropic nanoparticles with anisotropic nanoparticles on the surface has partially aligned magnetic easy axes on the surface and less complex magneto-crystalline anisotropy. This structure reduces the transverse contrast efficacy. In addition, the core-shell ensemble under consideration exhibits enhanced thermally dependent magneto-crystalline anisotropy due to the amalgamated impact of aligned easy axes of the shell and randomly oriented easy axes of the core. This property attenuated MR-transverse relaxivity. Based on these observations, we put forward a hypothesis for T_2-transverse contrast efficacy, proposing a correlation between easy axes orientation, collective magnetic behaviour, and complex anisotropy energy distribution landscape.

- Proton dephasing across a densely concentrated assemblage of nanoparticles demonstrating frustrated magnetic state transition is difficult to completely grasp. In such frustrated magnetic nanosystems, where the basic mechanisms guiding MR-relaxivity can no longer be established through saturation magnetization solely, it is necessary to analyse the underneath mechanism. By analysing the bi-magnetic ensembles of Zinc Ferrite nanorods and maghemite nanoparticles, we determine the contribution of magnetic anisotropy in controlling longitudinal and transverse MR-relaxivity. The emergence of a frustrated magnetic state in γ-Fe_2O_3@$ZnFe_2O_4$ results from competing spins and structural anisotropy induced by the mass fractal configuration of isotropic nanoparticles. The dynamic magnetic responses of spins regulate the energy barrier with a broad distribution, characterised by a spin reversal time of 1.2×10^{-8} s and an energy barrier of 8.2×10^{-14} erg. Additionally, the inhomogeneous field gradient is found to be governing the MR-relaxivity. Therefore, signal amplification is found to be responsible for devised dynamic responses, which accelerate the water proton decay during the MR-relaxivity process. The designed cell-viable bi-magnetic ensemble reveals an intriguing approach for improving r_2/r_1 through an extremely low

concentration of 0.1 mM and a low magnetic field of 1.4 T. However, shape anisotropy-induced MR-transverse relaxivity is emphasised by considering another interacting superparamagnetic hierarchical tri-magnetic ensemble, formed by flower-shaped tri-magnetic ensemble of two-dimensional flakes with nanoparticles, γ-Fe_2O_4@δ-MnO_2@$NiFe_2O_4$. By amended shape anisotropy, spin-blocking distribution, and energy barrier broadening, MR-transverse relaxation is found to be faster. In MR images, an incredibly efficacious MR-transverse relaxivity having a transverse (r_2)/longitudinal (r_1) relaxivity of 61.5 is exhibited, along with a suitable level of cell viability. Consequently, our investigation reveals a correlation between MR-transverse relaxivity and dynamic magnetic behaviours for a competitive terrain of hierarchical tri-magnetic ensembles. Hence, the larger size of the contemplated systems will outweigh the constraints of nanoparticles with fine dimensions.

- An overall comparison statement of MR-transverse relaxivity efficiency for the developed systems has been provided below in Tabular form as follows:

Table 9.1: A comparison of MR-relaxivity efficiency of the developed systems.

Systems	r_1 ($mM^{-1}s^{-1}$)	r_2 ($mM^{-1}s^{-1}$)	r_2/r_1
Isotropic Ensemble of $Ni_{0.75}Zn_{0.25}Fe_2O_4$@CoO	0.24	7.3	30
Isotropic Ensemble of $Ni_{0.5}Zn_{0.5}Fe_2O_4$@CoO	0.22	4.3	19.5
Compact Ensemble of Isotropic Zinc Ferrite (CEIZF)	0.41	31.8	77.5
Compact Ensemble of Anisotropic-Isotropic Zinc Ferrite (CEAIZF)	0.35	17	49.1

Compact Ensemble of Zinc Ferrite (CEZF)	0.39	28.9	74.2
Core-Shell Ensemble Zinc Ferrite (CSEZF)	0.31	16.7	53.6
Hollow Core Ensemble Zinc Ferrite (HCEZF)	0.28	21.9	78.4
Bi-magnetic ensemble γ-Fe_2O_3@$ZnFe_2O_4$	0.46	15.94	34.65
Tri-magnetic ensemble γ-Fe_2O_4@δ-MnO_2@$NiFe_2O_4$	0.27	16.67	61.5

The system hollow core ensemble of Zinc Ferrite shows the highest efficiency in MR-transverse relaxivity. In addition to shape, size, and saturation magnetization of the nanoparticles, the parameters that are found to have an impact on proton relaxation rates are: 1) Magneto-crystalline anisotropy, 2) easy axes alignment, 3) Exchange coupling, and 4) Spin density, which are mentioned in Chapter 5. The samples are designed to modulate the shape anisotropy expecting to show varied easy axes orientation. In complex structures as considered, an average field that the water proton experiences is not restricted to saturation magnetization, rather, easy axes alignment has appeared to be the characteristics since it can cause regulation in inherent properties. Furthermore, the predominance of exchange field has been identified, that affects the anisotropy landscape alongside the asymmetric coercivity. The improved MR-transverse relaxivity appeared with a stronger exchange field, more significant asymmetric coercivity having easy axes alignment, magneto-crystalline anisotropy reduction, as well as lower saturation magnetization. Instead of taking the shift in Larmor frequency into consideration to provide a more reasonable rationale for the contradicting results, such stable parameters pave

the way toward an understanding of proton relaxation modulation. The higher anisotropic landscape inhomogeneity that has been found offers a pathway for achieving faster water proton relaxation.

9.2 Future directions

- In this thesis, we have explored the dynamic magnetic responses in ensembles of spherical nanoparticles, nanorods, two-dimensional flakes, and dis-integrated nanorods. However, consideration of other assemblies of two-dimensional magnetic nanoflakes and integrated two-dimensional nanosystems to explore dynamic magnetic behaviour and various non-ergodic behaviour can be considered as a prime further direction.
- The slower spin dynamics of ensembles can be validated further by executing Monte-Carlo simulations of the developed ensembles for more detailed comprehension of the experimentally achieved anomaly.
- MR-relaxivity of various assemblies of two-dimensional nanoflakes can be studied and validation of the addressed hypothesis can be verified by considering different anisotropic nanosystems.
- For a more in-depth comprehension of the MR-relaxivity study, the structure-correlated MR-relaxivity can be addressed by analysing the Nuclear Magnetic Relaxation Dispersion (NMRD) profile in multiple frequency domains for the development of MRI-contrast media.
- In this thesis, the developed ensembles exhibit outstanding MR-relaxivity behaviour with excellent cell viability. Hence, to validate the real-time MRI applicability of the developed cell-viable complex ensembles, it is possible to conduct *in-vivo* experiments for medical practice.