Chapter 1

Introduction

1.1 Magnetic nanosystems

Magnetic nanosystems have exotic significance in a multitude of technological domains due to their captivating inherent behaviours [1-3]. Nanoscience continues to be dominated by the widespread interest in modifying the structural properties of nanomaterials to use its capabilities [4-8]. Because of their promising use in numerous scientific domains, the magnetic nanoparticles family has been the significantly researched materials [9-12]. Developing magnetic nanoparticles (MNPs) with tunable structural correlations has shown scientific attention because of specific inherent magnetic nature with special physiochemical properties [13-16]. Additionally, the advancement of nanotechnology has accelerated the progression of MNPs of metal oxides, providing such MNPs with unique magnetic behaviour [17-20]. It has also been demonstrated that MNPs' magnetic moment along with their anisotropy differ from their bulk counterparts [21-24]. Thus, research into structural properties is essentially important, especially for different applications as, data storage, biomedicine, etc. [5, 15, 25-27]. The dimensions of nanostructures have exactly the same order as that of the range of interactions, which describes magnetism. Thus, the behaviours obtained in nano-ranged materials vary from their bulk counterparts and exceptional magnetic behaviours are exposed. Hence, quantum theories are found to be more dominated in explaining properly the inherent physical behaviours of nano-level materials rather than that of classical theories. The multi-domain structure of MNPs is the result of magnetostatic energy stabilization, which relies on the volume of the system, relative surface area, and the competing energy related to the domain wall [28-31]. When MNPs' size is confined to a threshold scale, nanometre range, where sustaining of multidomain

structure is energetically unfavourable, it gives rise to single domain nanoparticles.

In fine ferromagnetic and antiferromagnetic nanoparticles having single domain structure, the magnetization possesses an orientation either parallel or antiparallel to a definite direction addressed as easy axis. Louis Néel introduces the concept of superparamagnetism [30, 32, 33]. In a single-domain system having uniaxial anisotropy, anisotropy energy density can be represented as, $E = KVsin^2\theta$ wherein θ angle between easy axes and magnetization. K denotes anisotropy constant and V is MNP volume. The parallel and antiparallel magnetization direction is separated by a ΔE (KV) which is known as an energy barrier. When the particle size is very fine, thermal energy can surmount the anisotropy energy. In such a scenario, even in zero external field, magnetization can switch suddenly from one easy axis to a different one. Like paramagnets, in an ensemble comprised of non-interacting single-domain fine ferromagnetic nanoparticles, a giant spin is formed due to the individual spin coupling which can arbitrarily flip in the easy axis direction even at room temperature [34]. When a diluted ensemble comprised of non-interacting nanoparticles is considered, individual nanoparticles having a high moment of 10^3-10^5 μ_B behave as a single 'superspin' with the paramagnetic type of nature identified as 'Superparamagnetism'. Below a typical temperature, known as 'Blocking temperature' (T_B), an individual NP's moment is found to get blocked to its easy axes because of minute thermal energy ($k_BT < KV$), forming a disordered ground state [35]. This ensemble of nanoparticles is referred to exist in a superparamagnetic (SPM) state. The entire magnetic moment in an SPM state can be defined as single giant moment. SPM nanoparticles frequently exhibit a preferential direction along the magnetization direction. It is expected that these nanoparticles exhibit an anisotropy in such orientations. When there is only one favoured direction, it is addressed as uniaxial anisotropy. The magnetization direction can arbitrarily flip in such SPM nanoparticles having uniaxial

anisotropy, resulting in an impact on thermal energy. Ideally, SPM systems should have sufficiently high saturation magnetization with zero coercivity and remanence, which is challenging to attain in the experimental landscape due to the existence of interparticle interaction among primary nanoparticles [32-35].

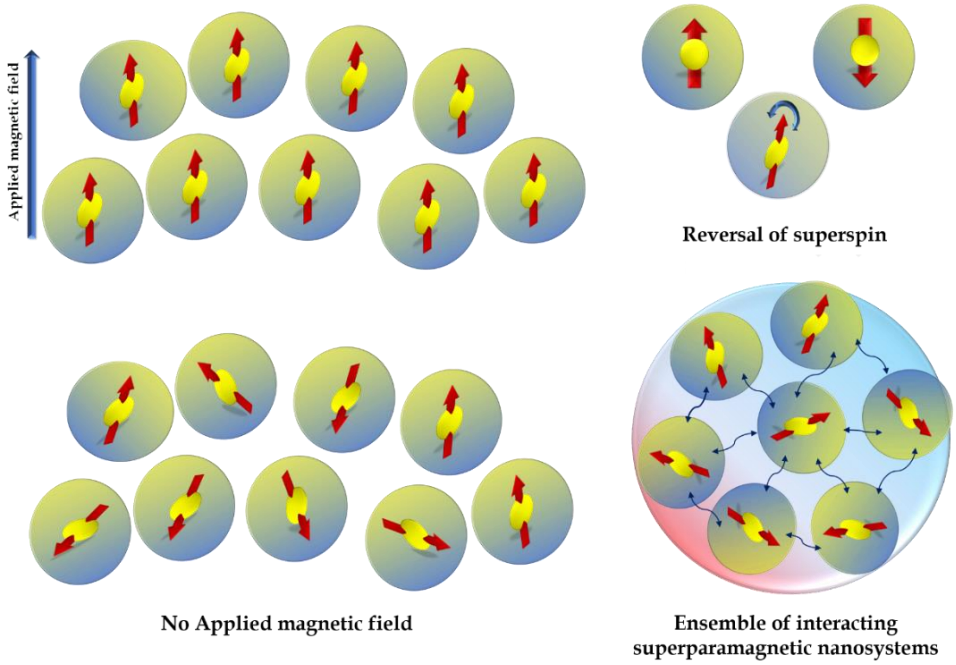

Figure 1.1: Schematic of SPM nanoparticles with no external applied field, with external magnetic field, reversal of superspin in non-interacting SPM nanoparticles, and an ensemble of interacting SPM nanosystems.

1.2 Ensembles of interacting nanoparticles

An ensemble comprised of single-domain nanoparticles retains the SPM behaviour when the primary nanosystems maintain a distinct interparticle separation. The variation in interparticle spacing leads to the evolution of varied kinds of interactions among primary nanosystems, which further leads to a collective magnetic nature [36, 37]. The energy barrier gets modulated due to the existence of interactions. In the ensemble of interacting nanosystems, the energy barriers of the ensemble get affected by the simple reversal of individual primary nanosystems [38-40]. The interparticle interaction strength is dependent on the

nanoparticles' volume in their ensemble. In such a scenario, the blocking of individual nanosystems is dominated by the interparticle interaction, which further results in collective spin freezing. However, size distribution and shape of primary nanosystems in their ensemble result in variation in magnetic moments resulting in complexity in magnetic behaviour. The influence of interaction in the magnetic phase in such ensembles can be understood by observing various low-temperature phase transitions such as the Superspin glass (SSG) phase, interacting superparamagnetic phase, superferromagnetic phase, etc. in such interacting systems [40-42]. Figure 1.1 shows a schematic of SPM nanoparticles with/without external applied field, reversal of superspin in non-interacting SPM nanoparticles, and an ensemble of interacting SPM nanosystems.

The interaction dominated in ensembles of nanoparticles are mainly dipolar interaction and various exchange interactions such as direct exchange interaction, Itinerant exchange, tunnelling exchange interaction, super-exchange interaction, Ruderman–Kittel–Kasuya–Yosida (RKKY) interaction, etc. as shown in Figure 1.2.

1.3 Various kinds of interaction

1.3.1 Dipolar interaction

In magnetic systems, the direct interaction of two separated magnetic dipoles is governed by magnetic dipole-dipole interaction [43-46]. The potential energy associated with the dipolar interaction is:

$$E = \left(\frac{\mu_0}{4\pi r^3}\right)[\mathbf{m_1}.\mathbf{m_2} - (3/r^2)(\mathbf{m_1}.\mathbf{r})(\mathbf{m_2}.\mathbf{r})] \quad (1.1)$$

Where $\mathbf{m}_1$ and $\mathbf{m}_2$ define the moments of the nanoparticles with a separation r between the moments and μ_0 stands for permeability of free space. The anisotropic long-range dipolar interaction relies on the degree of mutual alignment of moments and their respective distance [45]. In nanoscale magnetic materials, significantly large energy (of an order of 10^3 to 10^5 Bohr magneton) of

the moment is observed. Consequently, dipole-dipole interaction can have substantial effects on the behaviour of magnetic nanoparticles. An ensemble having randomly oriented nanosystems with moment μ and an average distance of r, dipolar interaction energy can be expressed as: $E_d = \frac{\mu_0 \mu^2}{4\,\pi r^3}$.

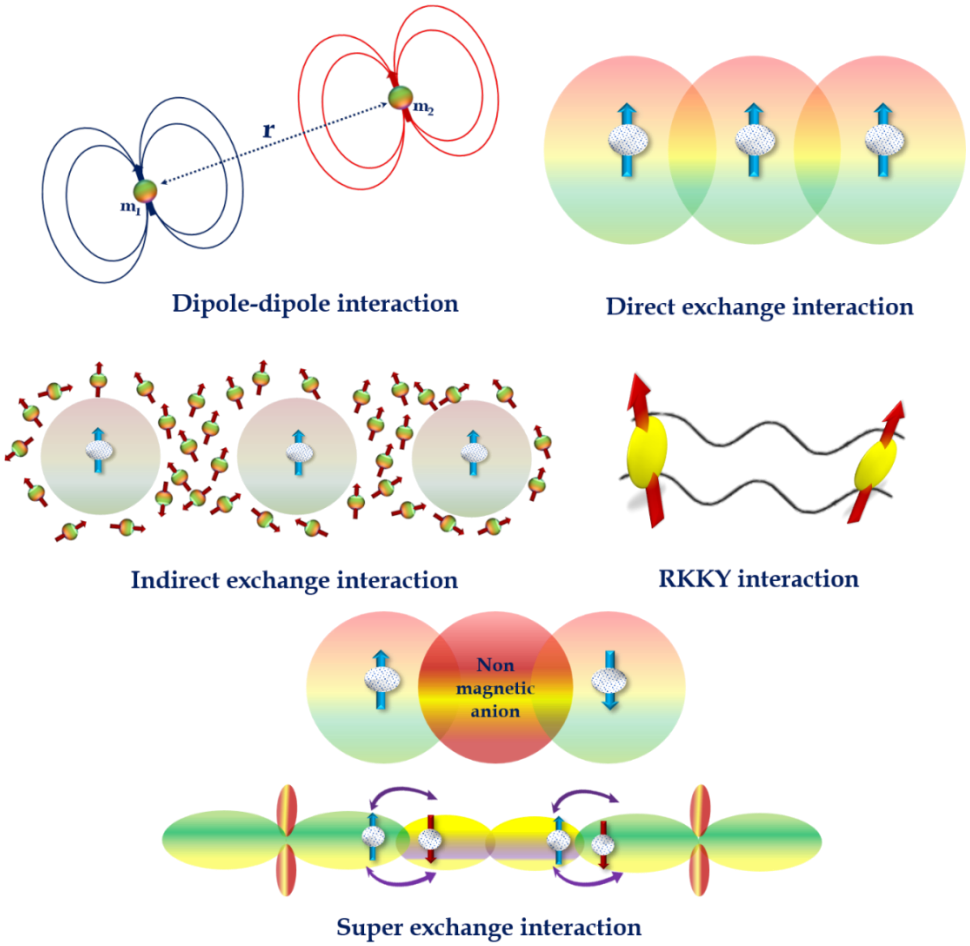

Figure 1.2: Schematic presentation of interactions types: Dipole-dipole interaction, Exchange interactions: Direct exchange interaction, indirect exchange interaction, RKKY interaction, and super-exchange interaction.

1.3.2 Exchange interaction and its various forms

The overlapping electronic orbitals of adjacent atoms give rise to exchange interaction and electron correlation is evident. In such interaction, the system's total energy is dependent on the spin orientation of adjacent atoms. Exchange

interaction can be regulated by various channels based on the system being considered [46-49]. As per the Pauli Exclusion principle, if the overlapping of adjacent atoms' electronic wave functions occurs directly, it is referred to as the direct exchange. The exchange energy related to two spin systems is equal to the difference of energy associated with parallelly oriented spin configuration and antiparallelly oriented spin configuration. Furthermore, the exchange of energy related to a many-electron system can be represented by Heisenberg Hamiltonian expectation value. In nanoparticles' ensembles, direct-exchange-interaction serves a vital role. In the framework of 3d metallic systems, exchange interaction arises because of delocalization of electrons and such delocalised electrons are named itinerant electrons. The exchange interaction due to delocalised electrons is known as itinerant exchange interaction. For magnetic property study in 3d metallic systems, electron band structure is important to take into account instead of considering coupling of atomic/ionic moments with inter-site exchange interaction. The band splitting of oppositely oriented spins arises because of Coulomb repulsion and kinetic energy associated with electrons, which results in the significant magnetic moment as a ferromagnetic state. Thus, the associated exchange splitting energy can be represented as the multiply of average atomic magnetization, M, with the Stoner exchange parameter, I. The Stoner criteria are followed to attain the magnetic order stability, which states that $IN(E_F) > 1$, where the Fermi level density of the state is expressed as $N(E_F)$. A metallic ferromagnetic state is attained due to strong exchange splitting as well as the high density of Fermi-level states.

The conduction electrons polarization leads to a different kind of interaction named indirect Rudermann-Kittel-Kasuya-Yoshida (RKKY) interaction. In RKKY interaction, the exchange integral exhibits an oscillatory nature because it alters signs depending on the gap that exists between localised moments. Generally, metallic nanoparticle ensembles exhibit RKKY interaction. The 4f electrons coupling of rare earth metals is solely because of RKKY exchange

interaction. In multi-layered GMR systems, RKKY interaction is liable for exchange coupling in the oscillatory interlayer. Additionally, RKKY interaction is a long-range interaction [48-50]. In transition metal oxides, exchange interactions are mediated by intermediate atoms/ions which triggers super-exchange interaction. Manganese Oxide (MnO) is a notable example of such super-exchange interactions. In MnO, the overlapping of 3d orbitals of Mn with 2p orbital of Oxygen, as well as partial delocalization of electrons enables interaction. The absence of delocalization happens because of moment orientation at the centres of metal, thus antiferromagnetic orientation becomes favourable. Generally, unlike exchange interactions of magnetic systems, super-exchange interactions are found to be long-ranged [46-50].

In SPM systems, the interactions of primary nanoparticles in an ensemble deviates the system from its ideal SPM nature. As a consequence, the collective magnetic behaviour of an ensemble can be explained by primary nanosystems' intrinsic magnetic nature along with the intensity of interparticle interaction [51-54]. Dipolar interaction and exchange interaction are the highly dominant kinds of interactions observed in such ensembles. In metallic magnetic nanoparticles, RKKY interaction is found to exist. In an ensemble, when the primary nanoparticles are in contact with each other, magnetic coupling arises among the nanoparticles via exchange interactions. This mimics the exchange interaction developed among the nearest neighbouring spins having ferromagnetic ordering. However, exchange interaction can arise for various collective magnetic states based on the geometry organization of nanosystems in their ensemble. In contrast, in most of the magnetic nanoparticles, dipolar interaction is observed to occur. When the nanoparticles are separated enough, the dipolar strength is found to be no more significant. The anisotropic behaviour of dipolar interaction leads to the development of some of exotic magnetic phenomena in highly interacting ensembles [53, 56, 57]. The evolution of super spin-glass nature and super-ferromagnetic states are examples of such behaviour [55-58]. If a

distinctly sufficient distance is maintained between two nanosystems, dipolar interaction dominates the collective behaviour. In solely dipolar interaction-dominated systems, the effect of interaction can be explained with the help of the Shtrikman-Wohlfarth (SW) model [9, 59], Dormann-Bessaic-Fiorani (DBF) model [38] and Mørup-Tronc (MT) model [39, 52]. An increasing trend of barrier energy with the aid of increasing interaction is believed by SW and DBF models. The Neel-Arrhenius relaxation equation is modified by introducing a term for interaction-dependent energy barrier, E_{in}, such as:

$$\tau = \tau_0 \exp\left(\frac{KV + E_{in}}{k_B T}\right) \tag{1.2}$$

This expression illustrates how the process of moment relaxation gets slower as interaction strength increases [52]. Moreover, the MT model specifies the inverse trend of moment relaxation with interaction strength. This leads to controversy in understanding the spin relaxation modification with interaction. Hence, in a highly interacting ensemble, when the organization pattern of primary nanoparticles, alignment in easy axes, and complexity in anisotropy provide an impact on energy barrier distribution modulation, the scenario becomes very complicated [60]. It is highly challenging to develop a theoretical model with controlled parameters such as distribution of fine particle size, precise particle dispersion, etc. Likewise, the degree of interaction can affect the coercivity and remanence of interacting ensembles. However, it is observed that the dependency of coercivity and remanence on the degree of interaction strength follows both increasing and decreasing ways [60]. Therefore, the degree of interparticle strength makes the ensemble very difficult to achieve a firm conclusion on spin-relaxation dependency. Sometimes the coexistence of more than one kind of interaction is found to be favourable in ensembles which results in more complexity.

1.4 Superspin glass phase

In highly frustrated ensembles of nanosystems, the formation of a glassy state is encountered. In a SG state, spins are frozen and orientation of the spins is random without maintaining any periodicity. Spin-glass phase is considered a different phase than that of long-range ferromagnetic and antiferromagnetic phases but shows familiar collective behaviour in their frozen state [61, 62]. In conventional spin-glass systems, long-range ordering is absent, unlike ferromagnetic/antiferromagnetic systems. In the case of magnets having a distinct order in the ground state, frustration in interactions arises due to the existence of quenched disorder, which develops on account of random interactions and vacancies. The correlation between cluster magnetism in ensembles and geometrical frustrations needs to be understood. To connect the cluster magnetism and geometrical frustrations, an assumption is drawn suggesting that the spin-lattice of frustrated systems is replaced by a network of spin-cluster. In the presence of discord in spin glasses, cluster mean-field (CMF) theory is needed [63]. It is assumed that the spin clusters interact among themselves instead of individual spin interactions. The self-consistent coupling of intra-cluster and inter-cluster parts results in instability in the glassy state. The geometrical frustrations can arise from the inter-cluster part taking into account an appropriate geometry of the inner cluster with antiferromagnetic interactions. However, a mechanism is employed for Ising spins with kagome geometry for stabilization of low-temperature cluster spin glass (CGS) phase having a weaker disorder in comparison to that needed for individual spins [64]. The mechanism is associated with the evolution of a classical spin liquid (SL) region, caused by a plateau observed in low-temperature entropy, that occurs before cluster spin glass instability. However, CMF theory states that cluster network is highly coupled and therefore cluster network connectivity plays an important role as a controllable parameter to draw the interplay between cluster magnetism

disorder and geometric frustration. The exact evaluation of the effect of connectivity variation of cluster networks on self-consistency is required.

In a system wherein magnetic elements are distributed in a framework of non-magnetic lattice, the transition from disordered to an ordered state is difficult. This results generation of a disordered system. At a specific temperature, such a system exhibits a state that is similar to a phase transition. Despite not being ordered, this state differs significantly from the high-temperature frustrated state [65-67]. The term 'glass temperature' (T_g) refers to such transition temperature where the mixed interactions enter a metastable frozen state with the absence of any general long-range order and the system is said to exhibit a SG state because of randomly freezing collective spins [61]. In the ensemble of interacting MNPs, SG type dynamics is also developed as a result of frustration brought on due to dipolar/exchange interaction and unpredictability in the MNPs placements along with alignment of anisotropy axes, similarly SG state observed in bulk systems. The term 'superspin glass state' (SSG) refers to the behaviours that occur in such interacting ensembles [62]. Although there exists an intermediately strong interaction, whether dipolar or exchange, among the domains in the SSG state, the direction of the individual domains remains frozen. The experiments based on frequency-dependent AC susceptibility, Direct current magnetizations, Field Cooling (FC) Memory effect, and Zero Field Cooling Memory (ZFC) effects are employed to ensure the SSG phase transitions in such interacting ensembles. Figure 1.3 shows a schematic representation of conventional SG freezing and cluster SG freezing.

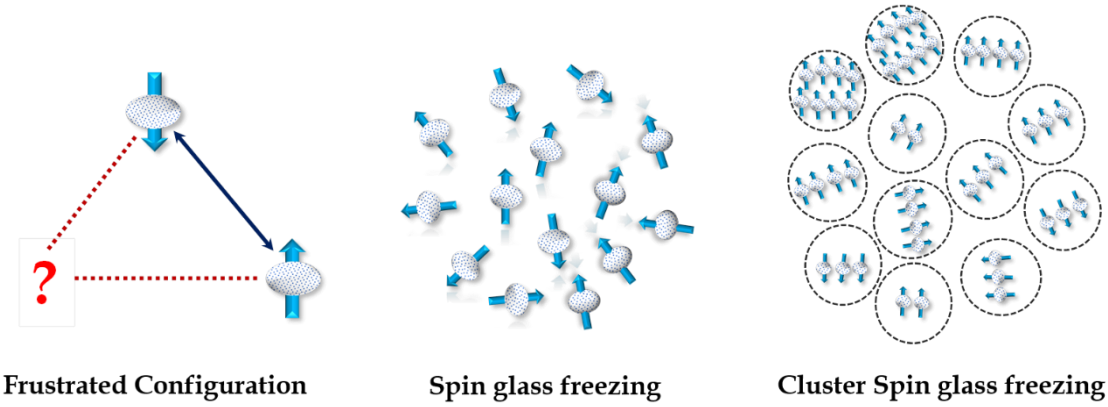

Figure 1.3: Schematic of frustrated geometry of antiferromagnetic spin, Conventional SG freezing, Cluster SG freezing.

1.5 Superferromagnetism

In 1983, superferromagnetism was addressed by Mørup during the Mössbauer spectroscopy experiment of microcrystalline goethite. In ensembles where the strength of the interaction is insignificant, the SPM state develops [58]. If the degree of nanoparticles' concentrations in the ensemble increases, the interaction becomes significant and collective freezing occurs in spite of single-particle blocking. At a higher degree of nanoparticles' concentration, a form of ferromagnetic (FM) domain develops with an increase in strength of interaction. Rather than individual atomic moments, superferromagnetism comprised of super-moments of entire primary nanoparticles develops in the ensemble. However, the Cole-Cole plot can distinguish the presence of SFM state and relaxation trends obtained from thermoremanent magnetic moment.

1.6 Quantum phenomena in ensembles of interacting MNPs

1.6.1 Non-ergodic behaviour

The disordered nanosystems are unable to reach their equilibrium, which results in slow spin relaxations with non-linear responses and time relying on nature. The magnetic frustration due to the complex free-energy landscape is the major

reason behind the evolution of such non-equilibrium behaviour. Certain temperature-dependent experimental techniques are present for deeper analysis of nonequilibrium dynamics of glassy systems. In spin glasses, temperature cycles are carried out to demonstrate the spectacular dynamical phenomena. Such temperature-dependent properties are addressed as magnetic memory effects, ageing, rejuvenation, etc. [68-70].

1.6.2 Magnetic Memory effect, Ageing and rejuvenation

Magnetic memory effect (MME) is a phenomenon where the system can remember its earlier history and can be unfolded under certain conditions. Several MME with time and temperature-dependent magnetization in various FC and ZFC protocols are observed in spin-glass, super spin glass, and interacting SPM systems [68, 69]. Such time (t)/temperature (T) dependent spin-glass magnetization illustrates the underlying spins arrangement and the quick relocation of spins to a favourable direction. It is proposed in non-interacting nanoparticles that the memory effect results from a wide particle size variety and relaxation periods. Nonetheless, the memory effect is additionally triggered by spin-glass/SSG nanoparticles as a result of significantly higher interparticle interactions. To explain SG state, two different views are considered. The primary view considers droplet model (DM) where the domains or droplets of connected spins grow with cooling. Later view is based on hierarchical model (HM), in which various quasi-equilibrium states are arranged a hierarchically in the domain of phase space. MME due to the intermittent cooling process of FC/ZFC can be analysed with the aid of DM. The DM believes that the spin domain can have two distinct equilibrium states that are linked together by universal spin reversal. The respective alignment of spins is very responsive to relatively tiny temperature perturbations at a range larger than a typical overlap length. This explains why, in contradiction to the experimental results, the growth of the domain resumes from overlap length following slight temperature changes such as cooling/heating. But, such a different response to heating/cooling is

consistent with hierarchical model as well. In accordance with the hierarchical model, which takes into account the merging of multi-layered structures with an increase in temperature, the ageing is solely initiated by raising the temperature; however, the effects of ageing are reversed after brief cooling. It is observed that to comprehend the basic mechanism, the absence of memory effects associated with transient heating in spin relaxation dynamics has been thoroughly explored on a variety of nanosystems both experimentally and theoretically. Although it is still challenging whether a certain model accurately captures the behaviour of spin-glasses, the DM and HM, (wherein DM is derived considering re-normalization group arguments and HM is developed from mean-field theory) provide satisfactory explanations for the majority of memory effect phenomena [69, 70].

Ageing is a straightforward result of extended relaxation time frames, whereas a hierarchical arrangement of the free-energy landscape is necessary for memory effects and rejuvenation [71, 72]. The harshness of the energy landscape in spin glasses can be perceived as a result of ageing. This results thermally triggered crossing of energy barriers, which causes gradual relaxation of the system towards lower states of energy, at which the system remains for an extended period. Both memory and rejuvenation demonstrate a remarkable sensitivity towards temperature variation (increasing/decreasing) in the SG ageing state [73]. A hierarchical ordering of metastable states concerning the temperature variation is a common interpretation. This model demonstrates a relationship between changes in temperature with metastable states' free energy landscape. As the temperature drops, a continuous split of these metastable states is observed resulting in few new steps. This model predicts that 'ageing' refers to the evolution of metastable energy levels at a definite temperature T. When the temperature drops below the glass transition point, the free-energy states continue to break off into several sub-valleys. When temperature drops from T to T-δT, the sub-divided valleys are divided by new energy barriers [74]. The

system subsequently rearranges itself to attain the optimal spin arrangement for that particular temperature. Such energy state breaking happens continuously and is unaffected by presence/absence of a weak field. The observed transitions in the experimental limit can happen among adjacent sub-valleys within the major valleys for a sufficient period. As a result, the main valley population remains unaffected and prior memory is retained. To return to the prior T-landscape while rewarming, the memory can be restored. The magnetization collected in SGs with a modest probe field while waiting at a specific temperature below T_G is frozen in both the cooling and heating conditions. Throughout this process, the spin arrangement shifts in a short period. In the absence of a field, spin-spin correlation length increases during a pause, and warming often causes a memory dip [74]. The experiment demonstrates that below SG temperature with no magnetic field, system can rearrange its spin configuration around its equilibrium at that temperature. Further cooling causes the freezing of the equilibrium state, which is revealed upon warming. It appears to be recalling its 'age' or addressing it as exhibiting MME. There are two potential causes of sluggish dynamics in MNPs, based on both theoretical and experimental results [70-74]. In SPM MNPs, the broad relaxation period distribution is considered to happen due to anisotropy energy barriers of moments. It is assumed to be the sole responsible factor for getting slow dynamics in weakly interacting sparse MNPs. Confirmation of spin-glass phase transition is being seen for highly interacting systems having a narrow distribution of size. The Edwards-Anderson model is used to investigate various types of MME and rejuvenation effects [75]. The 'sub-ageing' and 'end of ageing' mechanisms are also addressed to explain the origin of SG systems. In highly interacting MNPs' ensemble, the potential source of slow dynamics is due to collective SG dynamics. The strength of dipolar interaction between the MNPs with randomization in their orientations and anisotropy axes directions are the origin of such frustrations. One must employ the experimental methods used for spin-glass investigations to check spin-glass-like characterizations of such systems.

1.6.3 Magnetic Resonance (MR) relaxivity

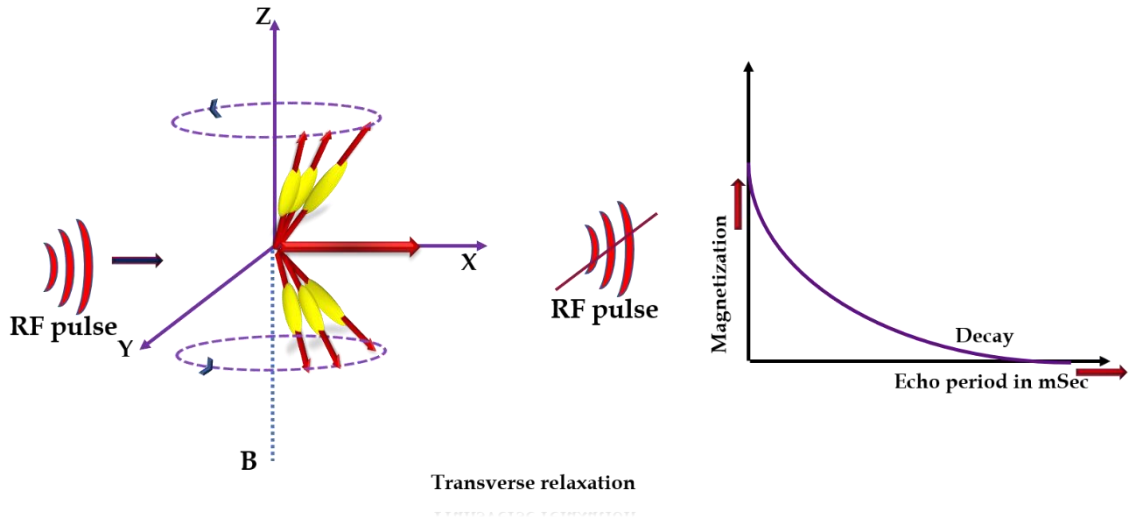

Figure 1.4: Schematic on transverse relaxation mechanism and decay period

Magnetic Resonance (MR)-relaxivity is also a quantum phenomenon which can be addressed by considering the enhancement of relaxation by MNPs relating to dynamic interaction between water protons and MNPs' magnetic centres [76]. Ensembles of MNPs having interparticle interaction can also influence the Magnetic Resonance (MR)-relaxation [77, 78]. The MR-relaxation of an excited magnetization state is understood by two different relaxations known as T_1 relaxation (spin-lattice relaxation) and T_2 relaxation (spin-spin relaxation). The T_1 relaxation provides information on how the energy dissipates to the molecular framework and the T_2 relaxation gives an idea about the correlation of energy dissipation to their neighbour atom configuration as shown in Figure 1.4 and Figure 1.5. The structural characterizations of MNPs in their ensembles are largely responsible for MRI-relaxivity enhancement. Consequently, because of the need for more rigorous control over the process of fabrication, due to the enhanced structural complexity, more specialised functional capacities are provided. However, the size of MNPs can impact the degree of magnetization of

MNPs as size can influence the variation of exchange interactions caused by various surface effects [76, 78].

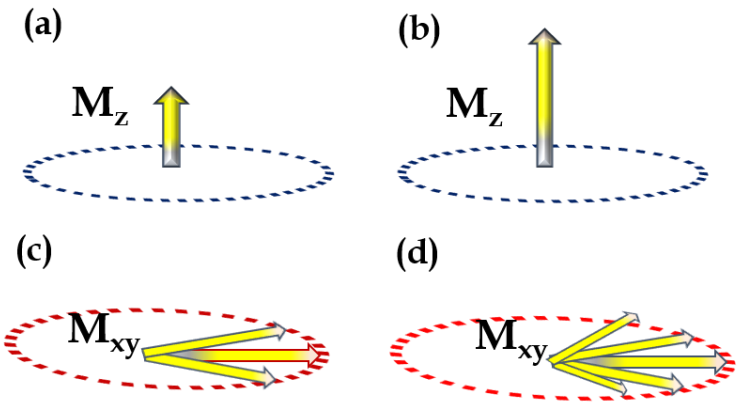

Figure 1.5: (a, b) Longitudinal relaxation enhancement, (c, d) transverse relaxation enhancement.

Additionally, because of the existence of shape anisotropy, the switching behavious of MNPs is closely correlated to the shape of MNPs [79]. Collectively, a need for elaborating understanding on structure relaxivity correlation with MNPs with MR-relaxivity is needed. It is observed that the outer-sphere quantum mechanical theory and Solomon Bloembergen-Morgon (SBM) model [76] have served as the basic principle to achieve an effectual efficiency in MR-relaxivity. While the enhancement of MR-relaxivity by an ensemble of MNPs with exquisite structural complexity is becoming more complicated, the traditional theories, which are developed based on oversimplification, are inadequate to explain the MR-relaxivity of complex ensembles.

1.7 Motivation behind the work

The collective freezing of isotropic iron oxide (IO) MNP assembly is investigated where freezing of spins is observed in frequency-dependent AC susceptibility and Field Cooling memory effect [80]. But MME is not prominently observed for all the low-temperature measurements. Therefore, a comparative study with further tuning of the interparticle spacing and the geometry of ensembles can be

investigated. In another approach, surface spin freezing has been found as the reason for development of SG characteristics in a hollow Maghemite nanosystem [81, 82]. Another attempt is observed where magnetic relaxation of fine nanoparticles ensemble is well explained with a non-interacting model, as disordered surface spins played a dominant role and effect of dipole-dipole interaction is considered to determine the magnetic behavior at low temperature [83]. With the increase in the size, an adequate section of spins showed bulk-like magnetization to cause collective properties via dipolar interactions and the spin relaxation of such interacting particles could be explained using the Vogel-Fulcher model. A different spatial arrangement of easy axes study is also investigated [51]. Fatty acid contribution for the tuning of the spatial arrangement of IO is observed. The relaxation of the spins is investigated by thermoremanence relaxation and Field Cooling memory effect analyses. Though systems are dominated by the dipolar interaction with varied strength, the clear understanding of the dipolar dependency on MME is still found as lacking [51]. It is still a controversial matter regarding the proper explanation of the origin of developed SG behavior whether it is a collective behavior resulting from interparticle interaction or freezing of randomly distributed surface spin, and it may be probable that both factors influence slow dynamics of real-time particles.

In the existence of dipole-dipole interactions, the alteration in the landscape of moment relaxation dynamics is a debatable subject [84, 85]. Initially, the Dormann-Bessais-Fiorani (DBF) model [38] portrays acceptable conclusions, which explain that an increase in strength of dipolar interactions leads to slower moment relaxation. There is an adequate number of experimental evidence to justify the aforementioned model [86, 87]. The influence of the dynamic interaction field, where the blockage and unblocking of moments were presumed in the laboratory time window, is explained by the assumptions addressed by the DBF model. Afterwards, Monte Carlo simulations support the validity of DBF model [88]. It is considered that, when local dipolar fields increase, anisotropy

barriers decrease, which triggers the growth of more and more microscopic energy barriers. As opposed to the DBF model, the Mørup model [39] demonstrates a faster relaxation period by interparticle interaction by considering a weakly interacting IO nanoparticle. Later in the DBF model, the phenomenological damping term is considered, which is an interaction-dependent parameter, to overcome the inadequacy. A flipping of moment is introduced by the Mørup model, where it is expected that the particles' moment prefers the easy direction. However, at high-temperature regions, where particles are in the unblocked state, this hypothesis will not be valid. This is due to the substantial probability of discovering the spins beyond the minima during an unblocked state. Hence, the DBF model is taken as an acceptable model to correlate the impact of interaction among SPM nanoparticles in an ensemble on energy barrier modulation. Nevertheless, in both the models, the impact of easy axes alignment and simultaneous complexity in an anisotropic energy landscape was not addressed, which may have a significant impact on energy barrier modulations.

However, the understanding of effect of size on MR-relaxivity is complicated, as the larger sizes of MNPs can affect the magnetic field, which results in higher transverse relaxivity [79, 76]. In the meantime, a positive correlation between the effect of magnetization and MNOs is also present. As a result, transverse relaxivity would be increased with an increase in MNP size supporting the traditional outer-sphere mechanism [89]. Fine MNPs with high surface-to-volume ratio having paramagnetism might develop into longitudinal (T_1)-dominant contrast behaviour in magnetic resonance relaxivity that benefits from reduced transverse (T_2) relaxivity. However, the shape effect plays a key role in adjusting the MR-relaxivity. Generally, compared to similar spherical nanoparticles, non-spherical-shaped MNPs have higher effective radii, which increases transverse relaxivity. Additionally, it is observed that star-shaped MNPs having higher T_1 relaxivity could be the result of elevation of second-

sphere contributions that are controlled by the shape [76]. However, the magnetization of MNPs is controlled by crystal structure leading to enhancement in relaxivity as stated by the earlier described conventional theories of T_2 relaxivity. When MNPs are surface-modified with a layer of magnetic/non-magnetic materials, additional parameters can be used to evaluate the T_1 and T_2 relaxivity with the coupling effect and behaviour of water protons diffusing around MNPs [90]. A straightforward yet incredibly efficient way to increase the T_2 relaxivity of MNPs is to assemble them from individual nanoparticles to clustered formations [91, 92]. MR-transverse relaxivity is linked to the behaviour of water molecules diffusing around the clusters such as the motional averaging regime (MAR), Static Dephasing Regime (SDR), and Echo-limiting Regime (ELR) [93]. The ensemble state, diffusion coefficient, multidomain structure of MNPs, and local field inhomogeneity are found as the four key factors that have complied from the diffusion behaviour of water protons and distribution of field surrounding the MNPs. With the increase in size, the possibility of an increase in saturated magnetization is expected which further complicates the evaluation of MR-relaxivity while attempting to examine a system's variables [76, 78]. This problem becomes more difficult when the considered system is multidomain with multiple crystal phases. In addition, structural modulation in the ensemble of MNPs of different sizes may have an impact on how the MR-relaxivity is handled. Only a handful of work is available where a single parameter is considered to explore the relaxation enhancement. Hence further investigation on dependable parameters to explain the mechanism of achieving a high MR-relaxivity is encouraged. Finally, the exploration of structure-relaxivity correlations has enormous potential for influencing the development of ensembles of MNPs to achieve highly efficient MR-relaxivity and for revealing the fundamental causes of novel phenomena of MR-relaxivity enhancement using ensembles.

1.8 Objectives of the thesis

The scientific disagreement can be resolved by introducing a few contributions about the interaction dependency on moment, such as, a) considering both randomly oriented easy axes and the impact of partial easy axes alignment on dynamics of spin relaxation along with blocking temperature variation; b) To calculate for relaxation period, the impact of demagnetizing field with dipolar field in interacting ensembles, iii) by taking into account various arrangement of single-domain nanoparticles in their ensembles and their inhomogeneous distribution, iv) surface phenomena in varied organized ensembles of both isotropic/anisotropic nanosystems, v) combined effect of dipolar and exchange interaction on spin-glassy phase. However, the limitations of structure-correlated complexity on MR-transverse relaxivity can also be addressed by considering the alignment of easy axes and complex anisotropy landscape in various geometrical arrangements of ensembles comprised of both isotropic/anisotropic nanosystems.

Considering all the aforementioned aspects, we have framed a few objectives as provided below:

1) The primary objective is to develop various geometry organizations with various spatial arrangements of both isotropic and anisotropic nanosystems. Isotropic ensembles of spherical spinal ferrite nanoparticles and ensembles of rod-shaped one-dimensional spinal ferrite nanosystems are considered. Two-dimensional flakes decorated over nanoparticles and resulting in a spherical ensemble are also considered.
2) Detailed structure-property investigation is performed for the ensembles of isotropic nanoparticles, one-dimensional nanorods, and two-dimensional flakes to ensure the structural behaviour correlation with the aid of Small Angle X-ray Scattering (SAXS) and Small Angle Neutron Scattering (SANS), and various microstructural studies.

3) The demagnetizing field-dependent spin-dynamics in varied geometry organization of ensembles of anisotropic nanoparticles is one of the major objectives of the thesis. Details understating the evaluation of MME with interaction strength are needed to investigate.
4) Interacting dependency on spin dynamic magnetic response in the ensemble of two-dimensional magnetic nanosystems is one of the objectives. Another objective is the realization of the impact of exchange field strength on low-temperature non-ergodic behaviours such as MME, ageing, etc.
5) Investigation on the role of interaction, domain of anisotropy landscape, and alignment in easy axes in Magnetic Resonance (MR)-transverse relaxivity considering magnetic ensembles of varied geometrical organization. We have also considered bi-magnetic and tri-magnetic systems to explore their impact on the MR-relaxivity mechanism.

References:

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