Chapter – 1

Introduction
1.1 Introduction to Nano-Magnetic Particles

Magnetic properties of the nanoparticles are the subject of intense research from the last decade [1]. In fact, microscopic structure of nanoparticles largely affects the macroscopic properties. Current research is devoted to tailor the microscopic properties at the nanometric scale and correlate it to the macroscopic properties like giant magneto resistance (GMR), and extraordinary Hall effect in metallic systems; large tunneling magneto resistance (TMR) in insulating glassy behavior and quantum tunneling of the magnetization [2]. In bulk magnetic material there exist multidomain structures constituted by region of uniform magnetization separated by domain walls (DW's). As the volume of the system decreases, the size of the domain and width of the walls decreases and hence magnetostatic energy decreases consequently, the inner structure of the system gets modified. Below certain critical volume, energy required to produce DW's is greater than the magnetostatic energy therefore, system will not further divide in domains but maintain the single domain structure. This critical size is defined as single domain (SD) size and it depends on the saturation magnetization of particle, anisotropy energy and exchange interaction between individual spins, i.e. for each system these values are different. In the case of a spherical particle the critical diameter is between 100-8000 Å [3]. Typical values for spherical metallic particles like Fe and Co are 150 Å and 350 Å respectively, while for SmCO$_5$ it is as large as 7500 Å [4].

In a nanomagnetic system, magnetic behavior of the particle surface differs from that of the core, because of the distinct atomic coordination, compositional gradients and, concentration and nature of the defects present in both region. Thus, the core usually displays a spin arrangement similar to that of bulk material while a very large disorder in the spin arrangement on the surface may result on magnetic behavior ranging from a dead magnetic layer to that of a spin glass like behavior. The competition between both the magnetic orders – surface and core - determines the ground state of the particle. The observed high-field irreversibility, high saturation fields, extra anisotropy contributions and shifted loops after field cooling (FC) process can be attributed to the core-to-surface coupling. Thus, the finite size affect largely to the magnetic response of the nanoparticles.
In a fine particle system, the volume of the particle is in the range of few tens or hundreds of Å³ and so it can be considered as ‘zero’ dimensional magnetic system. Magnetic behavior of a nanoparticle system depends on the size, size distribution and shape of the particles as well as on the anisotropy energies like size, shape, magneto crystalline etc., and on relaxation time.

When a magnetic material placed in a magnetic field of strength \( H \), the individual atomic moments in the material contributes to its overall response and the magnetic induction is given by,

\[
B = \mu_0 (H + M)
\] ..........................  (1)

Where,
\( \mu_0 \) = Permeability of the free space and
\( M \) = Magnetic moment per unit volume (\( \mu/V \))

In nature, all materials are magnetic to some extent and their magnetizations depend on their atomic structure and temperature. Therefore magnetization \( M \) induced in a material by an applied field \( H \) is given by a susceptibility \( \chi \).

\[
M = \chi H
\] ..........................  (2)

Figure - 1 shows response of different magnetic materials when placed in an external magnetic field. Susceptibility of the material can be derived form the slope of the line. For the different magnetic materials its values are as follows.

(a) Diamagnetic materials \( \chi_d \sim 10^{-6} \) to \( 10^{-3} \) (Figure -1(a))
(b) Paramagnetic materials \( \chi_p \sim 10^{-6} \) to \( 10^{-1} \) (Figure -1(b))
(c) Ferromagnetic materials \( \chi_f \sim 1 \)  (Figure -1(c))

In ordered magnetic states viz. ferromagnetic, ferrimagnetic and antiferromagnetic materials susceptibility of a material depends on magnetic field and temperature. In ferromagnetic and ferrimagnetic material hysteresis loop is observed (figure-1(c)). This
Figure 1: Typical diagram of the various magnetic materials when exposed in gradient magnetic field. Response of a (a) diamagnetic (DM) material and (b) paramagnetic (PM) materials when placed in external magnetic field. For the ferromagnetic materials the effect of particle size is shown in (c). Area under the curve for large particles is smaller than the small particles. While for the superparamagnetic (SPM) particles no hysteresis is observed (d).
is an irreversible process in the magnetization and for large particles (say μm or more), area under the curve of the loop is smaller (due to multidomain structure) compared to smaller particles (single domain). In the nanoparticles (<150 Å) [5], a new phenomenon is observed called super-paramagnetism (SPM), where the moment of the particle as a whole is free to fluctuate in response to thermal energy, while individual atomic moments maintain their ordered state relative to each other (figure-1(d)). The relaxation time, \( \tau \), to measure the thermal fluctuation of a particle is given by,

\[
\tau = \tau_0 \exp \left( \frac{\Delta E}{k_B T} \right) \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldOTS
vitro studies one has to obtain deeper insight into role played by the physical parameters like size, size distribution, magnetization strength and nature of biomolecules, coating on the particles etc. Among all these NMP also covers a broad spectrum of industrial applications like magnetic fluids (described in the next section); magnetic seals in motors, magnetic inks for bank chaques, magnetic recording media etc. As shown above for each potential application requires the magnetic nanoparticles to have different properties. For example, (i) in data storage application, the particles needs to have a stable, switchable magnetic state to represent bits of information, a state that is not affected by temperature fluctuations, (ii) in hyperthermia treatment, the particles should have low Curie temperature and so must be temperature sensitive.

<table>
<thead>
<tr>
<th>1. Structural</th>
<th>2. Biotechnology</th>
<th>3. Information and communication technology (ICT)</th>
</tr>
</thead>
<tbody>
<tr>
<td>* Ceramics,</td>
<td>* Nanoencapsulates,</td>
<td>* Single-walled nanotubes,</td>
</tr>
<tr>
<td>* Catalysts composites,</td>
<td>* Targeted drug delivery,</td>
<td>* Nanoelectronics,</td>
</tr>
<tr>
<td>* Coatings, thin films,</td>
<td>* Biocompatible materials,</td>
<td>* Optoelectronic materials</td>
</tr>
<tr>
<td>* Powders,</td>
<td>* Quantum dots,</td>
<td>e.g. TiO$_2$, ZnO, Fe$_2$O$_3$,</td>
</tr>
<tr>
<td>* Metals etc</td>
<td>* Composites,</td>
<td>* Organic light-emitting diodes (OLEDs) etc</td>
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<tbody>
<tr>
<td>* Microelectromechanical systems (MEMS),</td>
<td>* Nanofiltration,</td>
<td>* Metal oxides e.g. TiO$_2$, ZnO, Fe$_2$O$_3$, etc</td>
</tr>
<tr>
<td>* Nanoelectro- mechanical systems (NEMS),</td>
<td>* Membranes etc</td>
<td></td>
</tr>
<tr>
<td>* Scanning probe microscopy (SPM),</td>
<td></td>
<td></td>
</tr>
<tr>
<td>* Dip-pen lithography,</td>
<td></td>
<td></td>
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<tr>
<td>* Direct-write tools</td>
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</tr>
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1.2 Introduction to Magnetic Fluids

1.2.1 Basics

Magnetic Fluid (MF) is a colloidal suspension of single domain ferro or ferri magnetic particles coated with a monolayer of a dispersant and suspended in a magnetically passive medium [10]. The number density of nanomagnetic particles (NMP) in a MF is about $10^{17}$ cc. Magnetic fluid or ferrofluid reflects combine properties of magnetic and liquid state. In 1960's Rosensweig [10] has developed a new branch of hydrodynamics called "Ferrohydrodynamics" (FHD). The aim of this is to study the physical characteristics of MF. In MF using this dynamics several distinct phenomena like levitation, spike formation, formation of labyrinthine patterns in the thin layer etc. can be explained. Due to the uniqueness of fluid having the giant magnetic response ferrofluids are used in various fields for several of applications.

Stability of a suspension is affected by the following parameters: (i) Thermal energy ($k_B T$) - $E_T$, (ii) gravitational energy ($\Delta \rho V g L$) - $E_g$ and in case of magnetic suspension on (iii) magnetic energy ($\mu_0 M H V$) - $E_m$. Where $k$ is the Boltzmann constant, $T$ is the absolute temperature, $\Delta \rho = \rho_{\text{solid}} - \rho_{\text{fluid}}$, $V$ is the volume of the particle, $g$ is gravitation force, $L$ is the elevation in the gravitation field and $\mu_0$ the permeability of free space. The last two parameters can be manipulated in terms of volume of the particles. To keep the particles suspended, gravitational energy should be lower than the thermal energy. In magnetic fluid this condition is always satisfied. For example, in Fe$_3$O$_4$ ferrofluid, for the particle size range from 50 Å to 150 Å with $\Delta \rho = 400$ g cm$^{-2}$, $g = 980$ cm s$^{-2}$ and $L = 1$ cm; the gravitational energy ($E_g$) for 50 Å and 150 Å are $2.56 \times 10^{-22}$ g cm$^2$ s$^{-2}$ and $6.92 \times 10^{-21}$ g cm$^2$ s$^{-2}$ respectively. These values are two order of magnitude lower than the room temperature (~298 K) thermal energy i.e. $4.21 \times 10^{-20}$ g cm$^2$ s$^{-2}$. Therefore one can neglect the effect of gravitation energy for this range of particles in a ferrofluid. Thus for stability one has to considered the contribution of possible attractive forces and methods to overcome the same.
(i) Attractive forces

In the absence of external magnetic field, two man attractive forces exists between the magnetic particles in a ferrofluid. These are the (a) van der Waals-London and (ii) dipole-dipole interactions. For the spherical particles the van der Waals-London interaction, $E_v$, is written as,

$$
E_v = -\frac{A}{6} \left[ \frac{2}{l^2 + 4l} + \frac{2}{(l+2)^2} + \ln \left( \frac{l^2 + 4l}{(l+2)^2} \right) \right] \quad \text{............ (4)}
$$

Where $A =$ Hamaker constant and $l = 2s/D$ with $s =$ surface to surface separation distance and $D =$ diameter of the particle. This is a short range attractive force. A typical potential energy curve having different surface to surface distance is given in figure 2.

In magnetic fluids each single domain particle behaves as a tiny magnet. Therefore, dipole-dipole interaction exists between the particles. The dipole-dipole pair energy is given by,

$$
E_{dd} = \frac{\pi \mu_0 M^2 D^3}{9 (l+2)^3} \quad \text{.................. (5)}
$$

Where $\mu_0 =$ Permeability of free space and $M =$ magnetization of the particle. This is a long range attractive force. When $l=0$; thermal agitation disrupt the agglomerates. This is governed by the ratio of thermal energy to magnetic energy. For the stable colloidal suspension this should be greater than unity. Figure 2 shows the potential energy curve for 100 Å size magnetic particle.

(ii) Repulsive forces

In order to keep magnetic particle suspended one has to overcome these attractive forces. This is achieved either by providing Coulomb force or by sterically stabilize potential. Based on the type of potential used, the former is defined as ionic magnetic fluids and later as surfacted magnetic fluids [11-14]. In the thesis, we are only discussing about magnetic fluid which are stabilized by steric potential. This is given by,
\[
\frac{E_r}{k_B T} = \frac{\pi D^2 \xi}{2} \left[ 2 - \frac{l + 2}{t} \ln \left( \frac{1 + t}{1 + l / 2} \right) - \frac{l}{t} \right]
\] ......... (6)

Where, \( \xi \) = surface concentration of adsorbed molecules and \( t = 2\delta/D \) with \( \delta \) is the thickness of the adsorbed molecules. In figure 2, the effect of different coating thickness on the total potential energy is shown.

Various surfactants having polar adsorbing groups can be used for the coating of NMP, e.g. carboxyl, sulfoccusinate, phosphate etc [15]. Fatty acids have been widely used to stabilize colloidal dispersions of magnetic particles in both polar and nonpolar media [16]. In ferrofluid, the carboxylic head group binds the particle surface and hydrocarbon chain gives a hydrophobic sheath to individual dispersed particles. Steric repulsion is provided by the sufficiently long chains which results into a stable colloidal dispersion. In presence of excess surfactant a primary layer of magnetic particle may dissolved in the carrier liquid and hence agglomerate. It occurs, when loops or tails are associated with each other better than with the solvent. Usually, unsaturated fatty acids having chain length between C_8-C_{18} are
used as a surfactant in a magnetic fluid [17]. A Chemical structure of one such fatty acid, i.e. oleic acid, is given below.

\[
\text{Nonpolar tail} \quad \text{Polar head} \\
\begin{array}{c}
\text{\textbar} \\
\text{CH}_3 (\text{CH}_2)_8 = (\text{CH}_2)_8 \text{C OH} \\
\text{\textbar} \\
\text{O}
\end{array}
\]

Oleic acid coated magnetic particles are shown in figure 3. The polar head of the surfactant is adsorbed onto the surface of the magnetic particles either chemically or physically. The choice of the surfactant is very important because, in stable magnetic fluid the tail of the surfactant should be compatible to the surrounding liquid matrix. In magnetic fluid, when two particles approach each other surface-adsorbed layers are compressed and acts like elastic bumpers. This phenomenon is known as entropic repulsion.

Figure 3: Schematic sketch of the surface coating phenomena onto the magnetic particles with oleic acid as a surfactant.
**Net energy curve**

A net potential energy curve, which is an algebraic sum of the van der Waal attractive energy, magnetic (dipole-dipole) energy and steric repulsion energy, is shown in figure 2. For the minimum surface to surface distance, the net energy is dominated by the van der Waal attraction. However, on increasing \( l \), the net potential is dominated by the entropic repulsion. It is clear from the figure 1 that when the net interaction energy is greater than \( 25k_B T \), the fluid remains stable. For \( D = 100 \, \text{Å} \), this condition satisfy for \( \delta = 20 \, \text{Å} \) while fails for \( \delta = 5 \, \text{Å} \). Thus, it suggests that for the long term stability of magnetic fluid proper surfactant is required.

1.2.2 Properties of magnetic fluid

(i) Magnetic properties

In order to synthesize a magnetic fluid for a specific application, physical (rheological, optical etc.) and magnetic properties (magnetization etc.) of magnetic fluid should be tuned. These properties i.e. flow control, magnetization etc. are influenced by the external magnetic field. Therefore, the knowledge about the magnetic properties of magnetic fluid will be of the fundamental importance.

Magnetic fluid is a colloidal suspension of single domain nanomagnetic particles, where each particle is embedded with magnetic moment \( \mu \). In absence of external magnetic field, thermally agitated moments are randomly aligned and hence accomplishing zero net magnetic moment. Therefore for non-interacting monodomain particles the MF resemble a paramagnetic gas. Under the influence of magnetic field, magnetic moment aligns in the direction of external applied magnetic field, generating a net magnetic moment of a liquid like a ferromagnetic material. At very high field strength the particles may be completely aligned and the magnetization achieved its saturation value. This behavior is very well explained using the following classical Langevin’s equation for the non-interacting monodispersed particles.
\[ M = \frac{M}{M_s} = L(\alpha) = \text{Coth}(\alpha) - \frac{1}{\alpha} \quad \ldots \ldots \ldots \quad (7) \]

Where \( \alpha = \mu H/k_B T \). Depending on the preparation condition and the technique used MF may have distribution in particle moment (size). It is found that MF obeys log-normal size distribution function given by,

\[ P(D)d(D) = \frac{1}{D\sigma\sqrt{2\pi}} \exp \left[ -\left( \frac{\ln \left( \frac{D}{D_m} \right)^2}{2\sigma^2} \right) \right] d(D) \quad \ldots \ldots \quad (8) \]

Where \( \sigma \) = standard deviation of ln(D), \( D \) = particle diameter and ln(Dm) = mean diameter of ln(D).

**Figure 4a:** Theoretical M versus H plot for particle size \( D = 105 \, \text{Å} \) and \( M_d = 320 \, \text{emu/cc} \). Dashed line and solid line corresponds to monodispersed and polydispersed particles respectively, \( \sigma = 0.28 \).
Figure 4b: $M(H)$ curve for the Fe$_3$O$_4$ magnetic fluid. Solid line corresponds to theory and square corresponds to the experimental data points.

Considering the above equations (7) & (8), the Langevin's equation for the polydisperse magnetic fluid can be re-written as,

$$M = n \int_{0}^{\infty} \mu(D) L(\alpha) P(D) d(D) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldOTS(9)$$

Here, $n$ is the number density of the magnetic particles. Comparative theoretical curve for the monodisperse and polydisperse particles is shown in figure 4a. Figure 4b shows typical room temperature magnetization curve for the Fe$_3$O$_4$ magnetic fluid. The parameters derived from the fit (Eq. -9) are: domain magnetization $M_d = 320$ emu/cc, particle diameter (magnetic) $D_m = 105$ Å, size distribution $\sigma = 0.35$ and saturation magnetization $M_s = 49$ Gauss.
(ii) Magnetic relaxation

On removal of magnetic field magnetic particles relax back to its original position either by (i) Brownian or (ii) Neel relaxation mechanism. In the Brownian mechanism the relaxation occurs by particle rotation in a liquid matrix while in the Neel it is due to the rotation of the magnetic vector within the particle. For a single domain uniaxial ferromagnetic particles Neel relaxation (equation -3) is given by,

\[ \tau_N = \tau_0 \exp \left( \frac{\Delta E}{k_B T} \right) \]  

Where, \( \Delta E = KV \) = energy barrier to moment reversal, \( k_B T \) = thermal energy and \( \tau_0 \) = pre-exponential factor.

The particle rotation mechanism is characterized by a Brownian rotational diffusion time, \( \tau_B \), having hydrodynamic origin and given by,

\[ \tau_B = 3 V \eta_0 / k_B T \]  

Where \( V \) = Volume of the particle and \( \eta_0 \) = viscosity of the carrier liquid.

Above two equations [(3) & (10)] shows that the Neel and Brownian relaxation time depends on the size of the particle. On increasing particle size \( \tau_N \) increases exponentially while \( \tau_B \) increases linearly. In the case of magnetic fluids due to polydispersity of particle size, both the relaxation mechanisms are possible. The effective relaxation is given by,

\[ \tau_{eff} = \frac{\tau_B \tau_N}{\tau_B + \tau_N} \]  

For \( \tau_N << \tau_B \): Relaxation occurs by the Neel mechanism. Here anisotropy energy of the particle is greater than the thermal energy. This mechanism is also known as intrinsic superparamagnetic.

For \( \tau_N >> \tau_B \): Relaxation occurs by the Brownian mechanism. This mechanism is known as extrinsic superparamagnetic.
(iii) Viscosity

Rheology of magnetic fluids plays an important role to decide the suitability of a MF for particular applications. Since magnetic fluids are Newtonian in absence of magnetic field but in presence of external magnetic field the rheology is affected [18]. The following section describes the viscosity of the magnetic fluid for \( H = 0 \) and \( H \neq 0 \).

(a) Zero field viscosity \((\eta_H=0)\)

Commonly viscosity of the colloid is greater than the viscosity of the carrier liquid. Viscosity of a diluted colloid is given in terms of Einstein relation,

\[
\frac{\eta}{\eta_0} = 1 + 2.5\phi \\
\text{............. (12)}
\]

Here \( \eta \) is the viscosity of colloids, \( \eta_0 \) is the viscosity of the carrier liquid and \( \phi \) is the solid volume fraction. The above relation is valid for a diluted fluid while for a concentrated suspension modified equation is given as,

\[
\frac{\eta}{\eta_0} = \frac{1}{(1 + a\phi + b\phi^2)} \\
\text{............. (13)}
\]

For diluted magnetic fluid with \( a = -2.5 \) equation (13) reduced to equation (12). At critical concentration, \( \phi_c \), the fluid becomes effectively rigid and so the ratio \( \eta_0/\eta \) goes to zero. For this condition \( b = (2.5\phi_c -1)/\phi_c^2 \). Here, \( \phi_c \) represents the value of closest packing and for spherical particles it is equal to 0.74. In case of MF, each particles are coated with a surfactant layer of thickness \( d \) nm, which occupy a fractional volume \( \phi_h \) in the fluid given by,

\[
\phi_h = \phi_m \left(1 + \frac{\delta}{r}\right)^3
\]

Combining these relationships, equation (13) becomes,

\[
\frac{\eta - \eta_0}{\phi_m \eta} = 2.5\left(1 + \frac{\delta}{r}\right)^3 - \left(\frac{2.5\phi_c - 1}{\phi_c^2}\right)\left(1 + \frac{\delta}{r}\right)^6 \phi_m \\
\text{............. (14)}
\]

From the above equation and plot of \( \eta/\eta_0/\phi_m \eta \) versus \( \phi_m \) hydrodynamic size of the particle can be obtained. The slop (at \( \phi_m = 0 \)) and intercept (with \( \phi_c = 0.74 \)) of the equation gives the average diameter of particle and surfactant layer thickness, which agrees well with the particle size obtained from the other techniques, within the experimental error. This
equation is true only up to the critical concentration range $\phi_m = 0.3$, above this viscosity of magnetic fluid drastically increases. If the particles have a tendency to cluster, the value of $\phi_c$ reduced from 0.74. This results into drastic change in slop, leading to more significant difference between theory and experimental data.

(b) In-field viscosity ($\eta_H \neq 0$)

In-field viscosity measurement was first performed by McTague in 1969 [19]. The paper presents an effect of perpendicular and parallel field on the capillary flow. It shows that change in viscosity for the parallel configuration ($\Delta \eta_{||}$) is nearly double that in perpendicular configuration ($\Delta \eta_{\perp}$) [19].

Hall and Busenberg [20] developed a theoretical model but their predicted increments were significantly smaller than that observed by McTague [19]. Using the concept of the internal rotation Shliomis [21] gave the phenomenological equation of magnetization and derived expressions of viscosities for two configurations. Theoretical calculations of the viscosities agree well with those observed by McTague. Reduced rotational viscosity in the case $H$ perpendicular to the fluid flow direction ($\theta$), assuming all values of $\theta$ from 0 to $2\pi$, Shliomis gave the equation,

$$\frac{\eta_r^L(\alpha)}{\eta_r(\infty)} = \frac{3}{4} \phi \frac{\alpha - \tanh(\alpha)}{\alpha + \tanh(\alpha)} \quad \ldots \quad (15)$$

Where, $\alpha = \mu H/kT$, $\mu$ is the magnetic moment of the particle, $H$ is the applied field, $k$ is Boltzmann Constant and $T$ is absolute temperature. Afterwards, Felderhof [22] revised the conventional hydrodynamic equation, equation-14, using irreversible thermodynamics and proposed a following modified equation for the reduced rotational viscosity,

$$\frac{\eta_r^F(\alpha)}{\eta_r(\infty)} = \frac{9}{4} \phi \frac{L^2(\alpha)}{2 + 3L^2(\alpha)} \quad \ldots \quad (16)$$

Hall and Busenberg [20] have derived the condition for the saturation (limiting) value of reduced rotational viscosity and is given by $\eta_r(\infty) = 3\eta_\phi/2$. The rotational viscosities derived [23] from equations (15) and (16) are $\eta_r(\infty) = 3\eta_\phi/2$ and $\eta_r(\infty) = 9\eta_\phi/10$ respectively. Shliomis [23] has shown that former value of rotational viscosity does satisfy the condition given by [20] while later does not. He has observed that, 'local field'
considered in the Felderhof model can be replaced by effective field and hence gave a new
hydrodynamic equation as,
\[
\frac{\eta^{S_i}(\alpha)}{\eta_r(\infty)} = \frac{3}{4} \phi \left( \frac{\alpha L^2(\alpha)}{\alpha - L(\alpha)} \right)
\] ........................ (17)

Recently, Patel et al [24] have experimentally verified the theoretical equations given
by Shliomis [23] and Felderhof [22] for the reduced rotational viscosity. This study shows
that new hydrodynamic equation given by Shliomis[23] is in good agreement with the
capillary viscosity measurements of ferrofluids. Moreover, Patel et al [24] have also verified
this model by incorporating polydispersity in size. Thus it is also possible to derive the size
and size distribution from the field dependent viscosity measurement. Details of the zero
field and in-field viscosity measurements of certain magnetic fluids are given in chapter-3.

(iv) Optical properties

Since, magnetic fluids are opaque to visible light therefore, for the optical
measurements transparent samples are required. This is either done by diluting the sample or
by preparing thin film of MF. In zero magnetic field the ferrofluid exhibits isotropic optical
properties, but when polarized by magnetic field \(H\), it becomes optically uniaxial [25]. This
anisotropic behavior increases with increasing external magnetic field magnitude and
gradually approaches saturation. The single-domain magnetic particle size in magnetic fluid
is typically of the order of 100 Å and the wavelength of light used for magneto-optical
measurements is nearly 50 times greater. Hence the transmitted intensity will be governed
solely by single independent scattering. Due to their diverse phenomena, pattern forming
systems of ferrofluid films under external magnetic fields have attracted the interest of
scientists and engineers [26,27]. Theoretical explanation and experimental evidence of
optical birefringence, dichroism, extinction, relaxation and magneto-optical effects are
reported by many workers [28-42].

Optical properties of magnetic fluid having micron sized non-magnetic and magnetic
particles (i.e. microspheres) have been studied extensively [43-48]. In MF, interaction
energy between two spheres under first order approximation is proportional to \(H^2\) and may
easily be made comparable to the thermal energy. This offers a wide range of model systems
for experimental studies of phase-transition phenomena, e.g. systems with mixtures of different sized spheres forming a variety of crystalline and amorphous configurations [45]. When the non-magnetic micron sized particles are dispersed in magnetic fluids it behaves as magnetic hole under the influence of magnetic field [45].

1.2.3 Applications

A surfacted ferrofluid is a three component system viz. magnetic particles, carrier liquid and surfactant [10]. By varying the constituents, a wide variety of magnetic fluids with varying properties can be created. In MF carrier is a major component as fluid is referred by the carrier type. Moreover, another two important parameters of MF are saturation magnetization and viscosity. The former is magnetic property of solid magnetic particles and latter is a flow property of the carrier liquid. Applicability of MF is decided by these three components. Table-2 indicates some of the important applications of MF in engineering and biomedical/biotechnological field. For all these applications tailored particles having different properties are required. A large number of papers are available on the above aspects [7,49-55].

Biocompatible nanomagnetic particles have established their usefulness in several biotechnological and biomedical applications. Biocompatibility is achieved either by coating each individual particle with biomolecules like protein, dextran etc. or encapsulating a number of single domain particles in polystyrene or in a similar polymer. Each type has certain advantages over the other. For example in selective cell separation micron sized magnetizable polymer beads has been successfully used. These beads contain agglomerations being monodispersed the magnetic force will be uniform. While for applications like MRI contract enhancement, hyperthermia and targeted drug delivery it is found preferable to use single domain nanomagnetic particles coated with biocompatible molecules like dextran and PVA. The nanomagnets can also be functionalized by attaching molecules like carbodiimide which then facilitates the coating of protein or enzymes. Certain application like cell sorting and MRI contrast enhancement are commercially established but other auspicious applications like targeted drug delivery system, hyperthermia, tissue engineering etc. requited intensive research. For in vitro studies one has
to obtain deeper insight into role played by the physical parameters like size, size
distribution, magnetization strength and nature of biomolecules, coating on the particles etc.

**Table 2: Magnetic Fluids Applications**

<table>
<thead>
<tr>
<th>Engineering applications</th>
<th>Biomedicine and Biotechnological Applications</th>
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### 1.3 Introduction to Magnetic Fluids Composite

Study of magnetic fluid composite was initiated by Skjeltorp [44,45]. Where micron sized polystyrene spheres were dispersed in a magnetic fluid. Dispersion of nonmagnetic entity in a magnetic fluid, so-called magnetic fluid composite, have been studied for a long time [44]. This entities can be polystyrene spheres, magnetite particles, glass spheres [44,45,56] and also biological entities like TMV, TRV, Purple membranes, whole retinal rods, nuclei acids etc [57-61]. This is a new technique for the alignment of micron sized object dispersed in magnetic fluids. In this technique, magnetic forces cause the moments or spins of the magnetic particles to align along the direction of the magnetic field and their alignment, in turn, causes alignment of the dispersed assemblies. Such assemblies, which are to be aligned, have intrinsic diamagnetic moments and therefore can be align along the field
direction in the absence of magnetic particles but a very strong magnetic field is required. In contrast, the magnetic fluid alignment technique requires no intrinsic magnetic properties of the dispersed assemblies and only moderate field is required. This new technique involves the assemblies in a MF in external moderate magnetic field. The present work is concentrated on the following two systems. (i) Magnetic fluids - CTABr emulsion and (ii) Magnetic fluids- micron sized magnetic particle dispersion.

1.3.2 Magnetic fluid - CTABr emulsion

Surfactants are amphiphilic molecules in which part of the molecules is hydrophilic (likes water) and part of hydrophobic (fear water). In aqueous solution, surfactants aggregates into structures called micelles, where the hydrophobic portion of the molecules is protected from contact with water. Depending on the particular architecture of the surfactant molecules, a variety of microstructures can form. Possible aggregate structures are spherical micelles, warm like micelles, spherical vesicles, lamellar sheets or a variety of other topologies. The size and shapes of these micelles are studied using small angle neutron scattering (SANS) [62]. In order to minimize the free energy of the solution, the surfactant aggregates forms. As a result, they have dynamic (but equilibrium) structures, able to rearrange in response to change in environmental conditions. They also undergo thermal fluctuations and Brownian motion. Surfactant molecules are classified as ionic or non-ionic, depending on whether the head group has a net charge or not. The ionic surfactants are classified as Cationic e.g. Cetyltrimethyl Ammonium Bromide (CTABr) or Anionic e.g. Sodium Dodecyl Sulphate (SDS). Triton - X 100 is an example of a non-ionic micelles.

A preparation of stable emulsion of magnetic fluid with micelles will be of great interest, as this will give rise to the additional characteristic of magnetic behavior to the micellar solutions. The magnetic behavior of the micellar solutions will allow controlling the properties of micellar solution in the presence of magnetic filed if the micelles can be aligned. These studies are of importance as the micellar solutions are widely used in household, industrial and research applications [63]. Cetyltrimethyl Ammonium Bromide (CTABr), being a cationic surfactant, ionized in water. CTABr micelles are thus essentially aggregates of CTA$^+$ ions and micelle is positively charged. The Br$^-$ ion, referred to as
counter-ion, tend to stay near the surface of the micelle. Micellar solution of CTABr is isotropic at temperatures above 301 K in the concentration range of 0.001 M to 0.72 M. CTABr micelles are spherical at low concentration but become prolate shaped at higher concentration. In 0.1 M solution of CTABr, micelles are ellipsoidal (a ≠ b = c) and a/b ratio is 2.2 (where a is semi-major axis and b = c is semi-minor axis) [62].

Earlier in this laboratory, study of stable suspension of CTABr-magnetic fluid emulsions have been carried out [64,65]. This study showed that it is possible to use magnetic fluids to align CTABr micelles by applying the moderate magnetic field (figure 5). The system chosen was 0.1M CTABr + %y M Magnetic Fluids, where y = 5 to 30 % in step of 5%. These fluid samples were characterized using rheological, optical and Small Angle Neutron Scattering (SANS) measurements [64]. The study showed that for various concentrations of magnetic fluids viscosity increases linearly. The same behavior was observed using other techniques. Based on above results we have decided to study in detail characteristics of CTABr-magnetic fluid emulsions for various concentration of CTABr. Concentration above 0.1M CTABr, the micellar shape will be ellipsoidal and for lower concentration it will be spherical. Hence the present work was carried out for the lower concentration range. It is also aimed to examine the possibility of the alignment technique to align micelles in micellar solutions and to find whether the structural integrity of the micelles in a solution is disturbed due to the presence of magnetic fluid.

Figure 5: Deduced scattering patterns at (a) 303 K and (b) 333 K [64].
1.3.3 A composite: Magnetic fluids -- micron size magnetic particles

Magnetic fluid composite is a colloidal consist of stable suspension of 0.5-100 µm sized spheres (magnetic or non-magnetic) in a magnetic fluid. It has proved its useful as model systems to study many body phenomena in condensed matter physics [44, 45] as well as possible application like material separation [44,10]. In a zero external magnetic field a composite behaves as ordinary suspension. The holes created by the spheres appear to possess magnetic moment antiparallel to an external magnetic field at any field strength. The effective dipolar interactions between the spheres (holes) may make attractive or repulsive and varied relative to the thermal energy due to Brownian motion. The spheres are typically 100 – 1000 times larger than the uniformly distributed ferromagnetic particles in the magnetic fluid and the sphere will therefore move around in an approximately uniform magnetic background. As the magnetic fluid is ideally paramagnetic there will not be apparent magnetic interaction between the spheres in zero external magnetic field.

Skjeltorp [44] has reported the first direct microscopic observations of the crystallization of magnetic holes, which forms a variety of different lattices. He observed a phase transition phenomena in magnetic fluids – composites, i.e. a dispersion of non-magnetic micron sized polystyrene spheres and magnetic fluids.

Figure 6: Microscopic images of polystyrene spheres in a magnetic fluid film with 120 Oe parallel to external applied field. (a) High sphere concentration and (b) low sphere concentration [44].
Figure 6(a) and (b) shows typical ordered structures to the layer of different concentrations. In microspheres magnetic fluid composites three different phases exists. (i) a low-density or 'gas like' phase with isolated spheres and dimers; (ii) a medium-density or 'liquid like' phase with chain formation signifying attractive interactions between spheres and repulsive interaction between chains and (iii) a high-density or 'solid-like' phase signified by hard-sphere-like packing. Also, in rotating magnetic field nonlinear response of bound pairs of magnetic holes were also studied [46]. In the parallel and perpendicular external magnetic field [46, 66-68], light scattering study shows the formation of chain and structure formations. Dispersions of magnetic and nonmagnetic micron sized particles in ferrofluids also exhibit various order-disorder phenomena which could be explained using the concept of holes.

1.4 Basic motivation and objective of the present work

Finite-size effects dominate the magnetic properties of nanosized particles, and become more important as the particle size decreases. In many cases, they arise because of the competition between surface magnetic properties and core magnetic properties. The most obvious and heavily studied finite-size effect is superparamagnetism. The basic principle is that the magnetic anisotropy energy, which keeps a particle magnetized in a particular direction, is generally proportional to the particle volume. Therefore, at a given temperature there is a critical size below which thermal excitations are sufficient to rotate the particle magnetization, thus demagnetizing an assembly of such particles [69]. Superparamagnetism has been extensively studied in the nanoparticles of pure metals such as Fe, Co, and Ni [70]. However, the size of such superparamagnetic metal nanoparticles is confined within a few nanometers. In addition, these metal nanoparticles are chemically unstable. Thus, their applications are very limited. On the other hand, many magnetic metal oxides offer great opportunities for developing superparamagnetic nanoparticles with desirable properties. The nanoparticles of metal oxides such as spinel ferrites possess great potentials for applications since they are relatively inert and their magnetic properties can be finely tuned by chemical manipulations.
Spinel ferrites crystallize to a cubic closed-pack structure of oxygen ions in which tetrahedral (A) and octahedral (B) interstitial sites are occupied by cations. The site occupancy is often depicted in the chemical formula as \((M_{1-x}Fe_x)[M_xFe_{2-x}]O_4\), where round and square brackets denote the A and B site respectively, M represents a metal cation, and x is the inversion parameter. The origin of their magnetic properties is the spin magnetic moment of the unpaired transition metal 3D electrons, coupled by the superexchange interaction via the oxygen ions separating them. The strength of this short range interaction decreases as the distance between the magnetic ions increases, and also as the angle of the M–O–M bonds decreases from 180° to 90°. Accordingly, it has long been known that the A–O–B exchange sites interaction \((J_{AB})\) is much stronger than the B–O–B \((J_{BB})\) and the A–O–A \((J_{AA})\) interactions. Thus, the magnetic ions on the tetrahedral and octahedral sites can be considered to be ferromagnetically coupled within each sublattice, and antiferromagnetically coupled between the sublattices. Properties observed in nanoferrites are superparamagnetism, domain magnetization, Curie temperature etc. These properties can be modified by substituting diamagnetic ions such as, Cd and Zn, in ferrimagnetic spinel ferrites. One such study using Zn ion in MnFe\(_2\)O\(_4\) system was carried out by our group and found a potential candidate for a temperature sensitive magnetic fluid [71, 72]. The only difference between these two ions is ionic radius (Zn: 0.63 Å, Cd: 0.97 Å). Therefore it is of interest to observe the effect of ionic radius on the properties of MnFe\(_2\)O\(_4\). Although the magnetic properties of such system exists in bulk but few literature exists on nanoparticles [74-76].

According to Hasting & Corliss [73], micron sized cadmium ferrite has a normal spinel structure with Cd\(^{2+}\) and Fe\(^{3+}\) ions occupying the tetrahedral A-sites and octahedral B-sites, respectively. It exhibits an anti-ferromagnetic behavior due to B-B magnetic coupling. In contrast, for nanosized magnetic particles, Yokoyama et. al [74] have observed at 6K a saturation magnetization of 80 emu/g and hysteresis loops up to room temperature. Two different types of spin structure were suggested to explain these observed properties, i.e. (i) a core shell spin structure with a ferromagnetic core and inactive magnetic shell and (ii) non-collinear spin arrangement over the particle volume. Chinnasamy et. al [75] using high field Mössbauer spectroscopy technique showed that the cadmium ferrite behaves as mixed spinel on reducing the particle size (< 600 Å) and exhibits ferrimagnetic ordering with canting at
both the A and B sites. However, Mahmoud et. al [76] have shown recently that in cadmium ferrite A-site spins are collinear and only B-site moments are canted. They also show that the evolution from an anti-ferromagnetic ordering to a complex magnetic state (characterized by a local canted structure) is due primarily to small inversion of Fe$^{3+}$ magnetic ions in cadmium ferrite.

Several techniques are used to synthesize cadmium ferrite [73-78] particles. In all the above investigations the bulk cadmium ferrite samples were prepared using double sintering ceramic technique. In this technique stoichiometric mixture of pure iron oxides and cadmium oxides are mixed and calcined between 900-1000 °C for a few hrs. After this pre-calcination the powder is palletized and sintered at 1000 °C for more then 15 hrs. In order to get fine particles bulk sample is ball milled using high energy ball milling technique. The degree of inversion starting from the normal spinel increases with ball milling time. Furthermore in the above studies the particle size distributions vary from nano to micron-sizes, and the whole procedure is time consuming to say the least. These results motivate us to synthesize nanosized cadmium ferrite which should possess bulk properties. This is possible only if preparation is done at low temperature (1000 °C or lower). The low temperature synthesis of cadmium ferrite may help to synthesize mixed ferrites which aids to lowering the Curie temperature of the magnetic particles. The successful synthesis of ferrites using this method may render interesting industrial applications. From the above results, we have decided to synthesize cadmium ferrite having bulk properties and size < 1000 Å.

1.4.1 CTABr - magnetic fluid emulsion

Magnetic fluids are used successfully to orient biological assemblies such as tobacco rattle viruses (TRV) [57]. This new alignment technique involves the assemblies in a MF and applies moderate field. The present work examines whether MF mixed with the soft cetyltrimethylammonium bromide (CTABr) micelles can have any significant effect on flow behavior of the mixture under an applied magnetic field? Micelles are aggregates of surfactant molecules and these aggregates are usually formed in different shapes and size viz. spherical, cylindrical, ellipsoidal, disk-like, etc. CTABr, being a cationic surfactant ionizes in water. CTABr micelles are aggregates of the CTA$^+$ ions and they are soft and positively charged. The Br$^-$ ion, referred as the counter-ion, tend to stay near the surface of the micelle.
Micellar solution of CTABr is isotropic at a temperature above 301 K in the concentration range of 0.001–0.72 M. CTABr micelles are spherical at low concentration but become prolate shaped at higher concentration. In 0.1M solution of CTABr, micelles are ellipsoidal \((a \neq b = c)\) and \(a = b\) ratio is 2.2 (where \(a\) is the semi-major axis and \(b = c\) is the semi-minor axis) [57, 62]. These micelles are soft and they grow to ellipsoidal and rod-like micelles on addition of salts such as NaSal, KBr and KCl [62]. In the present work the zero field and in-field rheological properties of pure water base MF and stable CTABr MF emulsions (i.e. a suspension of droplets of one liquid in another liquid) for varying CTABr concentrations are described. The study is carried with an aim to understand the type of interaction exists between CTABr and magnetic fluid.

1.4.2 Biocompatible magnetic nanoparticles

Biocompatible nanomagnetic particles have established their usefulness in several biotechnological and biomedical applications [7]. The possible use of nanomagnetic particles in biomedical applications strongly depend on whether these particles are used for \textit{in vivo} (inside the body) or \textit{in vitro} (outside the body) applications. For \textit{in vivo} applications like, hyperthermia, drug delivery, magnetic resonance imaging (MRI), etc., magnetic particles must be coated with biocompatible polymers like dextran, protein, poly vinyl alcohol (PVA), poly ethylene glycol (PEG), etc. These polymers allow binding of drugs by covalent attachment, adsorption or entrapment on the particle. The biocompatibility and toxicity of these materials mainly depend on:

(i) \textit{Nature of the magnetic particles:} for example Fe\textsubscript{3}O\textsubscript{4} and \(\gamma\)-Fe\textsubscript{2}O\textsubscript{3} are most commonly used magnetic materials for biomedical applications. But magnetic materials like Fe, Co, Ni, etc which are susceptible to oxidation and toxic, are of very little interest.

(ii) \textit{Final size of the particles:} The final size includes core particle plus the surface coating. The nano size will have higher effective surface area. Therefore it provides greater probability of ligands attachment to particle surface.

(iii)\textit{High magnetization values:} This helps their movement in blood vessels; as a result it will be easier to immobilize them near to the targeted tissue.
The criticality of particle size is not that severe for in vitro applications like, cell separation and selection, magneto-relaxometry, etc. Therefore, one can use composite having superparamagnetic (SP) nanomagnetic particles dispersed in micron size dia- or-para-magnetic matrix. The advantage of diamagnetic matrices is that the SP composite can be easily provided with functionality. The use of nanomagnetic particles for MRI, cell sorting are commercially established but applications like targeted drug delivery system, hyperthermia, tissue engineering, etc., require intensive research.

In almost all applications the most important part which one has to address is the method of preparation, which should give high reproducibility and nearly monodispersed particle size. In addition, the preparation method determines to a great extent the surface chemistry of the particles, the degree of structural defects or impurities in the particle, as well as the distribution of such defects within the particle and therefore its magnetic properties. The aim of the present work is to develop magnetic nanoparticles for in vivo studies in particular for the hyperthermia and MRI. In most of the work carried out in these fields, magnetite or maghemite particles are used for the study, while alternative magnetic carriers are being less studied. In this thesis a comparative studies of nanomagnetic systems using magnetite and an alternative magnetic carrier Mn-Zn particles are reported. The choice of Mn-Zn nanoparticles is based on our earlier investigation that Mn-Zn particles are potential candidate for magnetic hyperthermia treatment [77, 78]. These particle surfaces are now functionalized by biocompatible molecules of citrate and dextran. In thesis characterizations of these particles using different experimental techniques are discussed.

1.4.3 Rare earth Ho doped magnetite magnetic fluid

The bulk magnetism of magnetic fluids is only of minor importance in most medical and biological applications. Here, the properties of individual particles dispersed in a fluid are more relevant. However, the magnetic properties of the individual particle strongly
depend on its volume, shape, magnetic moment, etc. Magnetite (Fe₃O₄) nano particles are most commonly used magnetic materials for the application in biotechnology and medicine because of their low toxicity and high magnetization values. In particular, magnetic fluid hyperthermia (MFH), in which, under alternative electromagnetic field irradiation of the particles transform the energy of the AC field into heat. The transformation, efficiency strongly depends on the frequency of the field, amplitude as well as the properties of the magnetic particles. Obviously, the physical and magnetic properties of the magnetic particles are crucial for the effectiveness and reliability of tumor therapy.

In the present work our aim is to synthesize and characterize the magnetic properties of rare earth Ho ion doped Fe₃O₄ magnetic fluid. The motivation for this is the results of our recent studies on syntheses and magnetic properties of Gd doped Mn-Zn magnetic fluid as a potential candidate for the magnetic fluid hyperthermia [77, 78]. In MFH the mechanism of loss is dominated by Neel relaxation and it increases with the increase in Neel relaxation time τ_N [79, 80]. The substitution of rare earth metal plays an important role in determining the magneto-crystalline anisotropy in 4f-3d inter-metallic compounds. In view of the above in we have carried out the synthesis of stable Ho-substituted Fe₃O₄ magnetic fluid and its physical and magnetic properties.

1.4.4 Micron sized magnetic particles dispersed in MF

In magnetic fluids, diffraction rings have been reported by several authors [81, 82]. In this diffraction pattern is attributed to the formation of micron sized columns. Tengda et al [47], have first time observed the diffraction rings in magnetic fluids having single domain nanosized particles. Figure 7 shows the ring patterns in zero magnetic field and at 12 Oe magnetic filed and also diffraction pattern in absence of focusing lens. The observed diffracted rings they have attributed to the thermal lens effect [83]. The similar behavior for the other liquid samples (not having magnetic or any other particles) has been observed by Gorden et al in 1965 [84]. The reason for is that due to laser beam focused (using the lens) on the sample absorbed the red light which increases the thermal temperature of the sample as well as change the refractive index of the sample.
Figure 7: Steady state diffraction patterns and thermal lens effects (a) $H = 0$ Oe, (b) $H = 12$ Oe. (c) On removal of focusing lens the phenomena disappears at $H = 40$ Oe [83].

Figure-8: Diffraction pattern of micron sized magnetite particles dispersed in a MF at different magnetic fields [68].
Afterwards, Tangda et al [83] have explained this non linear optical (NLO) effect on the basis of cross coupling between the temperature of the system and the concentration of the particles, which originates form the thermophoresis (i.e. particle migration along the temperature gradient). Field and time dependent diffraction pattern (in usual MF - mean diameter of particle is ~ 90 Å) has been observed for the different temperature and for various concentrations of particles. The observed field induced diffraction is attributed to the interaction between the magnetization of the fluid and the magnetic field gradient, originated from the inhomogeneity of both temperature and particle concentration. The obtained results suggest that the heat and particle transfers in colloidal fluids could be monitored and controlled by an external field.

Recently, our group has observed an unusual diffraction effect in dispersion of magnetic particles in a ferrofluid [68]. The sample consists of 3- micron sized magnetite particles stabilized by the surfactant and dispersed in a magnetic fluid. Result shows that, the diffraction pattern completely disappears at a particular magnetic field [68] (figure 8). On further increase in the field the pattern reappears. But, the reason for the complete disappearance was not clear. So as to get better understanding of this phenomenon some more experiments were needed. Thus, we have decided to study in detail characterization of magnetic fluid composite for various concentrations of micron size particles and tried to understand the phenomena of disappearance.
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