DOCTOR OF PHILOSOPHY

Radio Frequency Heating of Magnetic Perovskite Nanoparticles in Solution for Biomedical Applications

Cook, James

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Radio Frequency Heating of Magnetic Perovskite Nanoparticles in Solution for Biomedical Applications

A thesis presented upon application for admission to the degree of
Doctor of Philosophy
in the Faculty of Engineering and Physical Sciences
by

James Cook
MEng (Hons) 2015

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05/04/2019
Abstract

Magnetic nanoparticles (MNPs) are widely used in many different sectors especially within biological applications for heat generation or as contrast agents in magnetic resonant imaging. Our research concentrates on the magnetic susceptibility of MNPs and the effect on heat generation applications for use in biomedical applications as an alternative to invasive treatments such as chemotherapy.

In this thesis we have studied the response of clusters and chains of magnetic nanoparticles in solution. In particular we have focused on chains of MNPs that form through the spontaneous agglomeration of clusters. We are interested in magnetic response of MNP chains and how the response of the MNPs change with increasing chain lengths and different particle sizes.

To understand the response of MNPs we have implemented the stochastic-Landau-Lifshitz-Gilbert equation in the high friction limit to study their rotational magnetic response. We have modelled chains of dipolarly coupled MNPs up to twenty particles long and two different sizes of MNP (10 nm and 20 nm radius particles).

We have found that chains of MNPs show at least two resonant frequency modes and a marked deviation from the response predicted by a simple rigid body model. In particular the high frequency rotational response of the chain shows a crossover between the rigid body coherent response to an incoherent independent particle response. Implications to the specific absorption rate and heating capabilities of these chain are finally discussed.

The code implemented during this doctoral project has been made available from https://mangocode.gitlab.io.
I may not have gone where I intended to go,
but I think I have ended up where I needed to be.

DOUGLAS ADAMS
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Nomenclature

⌊ ⌋ Floor function, page 55
\(\alpha\) in x,y,z of primary Coordinate system, page 23
\(\beta\) in x,y,z of secondary Coordinate system, page 23
\(\gamma\) in x,y,z of tertiary Coordinate system, page 43
\(i\) of particle \(i\), page 22
\(j\) of particle \(j\), page 22
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\(s\) Indices of the unskipped time steps, page 41
\(i,\alpha, j,\beta\) of a single axis of a single particle, page 27
\(ij\) between particles \(i\) and \(j\), page 22
\(\prime\) First temporary quantity, page 26
\(\prime\prime\) Second temporary quantity, page 26
\(\prime\prime\prime\) Third temporary quantity, page 26
\(\ast\) Imaginary part, page 40
\(\bar{\text{\text}}\) Average of quantity, page 40
\(\tilde{\text{\text}}\) Fourier transform of property, page 40
\(\alpha\) Dimensionless friction constant, page 25
\(R\) Aspect ratio of a prolate spheroid, page 36
\(A\) Propagation time, page 39
\(A, B, C\) Directional cosines, page 16
\(a, b, c\) Length of ellipsoidal semi-axes, page 35
\(\text{BOX}\) Periodic boundary dimensions, page 55
\(\chi\) Magnetic Susceptibility, page 3
\(\chi_0\) Static Magnetic Susceptibility, page 34
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<tr>
<td>$K$</td>
<td>Cubic Anisotropy factor</td>
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<td>$M$</td>
<td>Scalar of total magnetisation of MNPs</td>
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<td>$m$</td>
<td>Magnetic moment</td>
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<td>$m_{\text{sat}}$</td>
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<td>$m_\rho$</td>
<td>Magnetic density</td>
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<td>$m_{\text{NP}}$</td>
<td>Mass of the particle</td>
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<td>$n$</td>
<td>Anisotropy axis</td>
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<td>$N$</td>
<td>Number of particles</td>
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<td>$N_b$</td>
<td>Number of blocks</td>
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<td>$N_n$</td>
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<td>$N_{\text{mag,corr}}$</td>
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<td>$\omega$</td>
<td>Angular velocity</td>
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<td>$\phi$</td>
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<td>$\phi_{\text{an}}$</td>
<td>Angle of the anisotropy axis to the external magnetic field</td>
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<td>$\rho$</td>
<td>Density</td>
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<td>$\rho_{\text{mag}}$</td>
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<td>Heat dissipated</td>
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<td>$p_{\text{therm}}$</td>
<td>Thermal momentum</td>
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<td>$p$</td>
<td>Vector momentum</td>
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<tr>
<td>$q$</td>
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$Q_{si}$ Heat Sink, page 4
$Q_{so}$ Heat Source, page 4
$\mathbf{R}$ Rotational Matrix, page 44
$R$ Scalar from rotational Matrix, page 44
$r$ Vector position, page 22
$r$ Scalar position, page 27
$\hat{r}$ Euclidean distance, page 22
$\hat{r}$ Magnitude of Euclidean distance, page 22
$r_{\text{pbc}}$ Minimal image MNP positions, page 55
$r_c$ Critical Radius, page 2
$\sigma$ Notional distance, page 31
$\sigma_p^2$ Population variance, page 41
$S$ Singular value decomposition (SVD), page 43
$S$ Indices of the time steps, page 41
$\boldsymbol{\tau}$ Torque experienced by a magnet, page 1
$\tau$ Time step, page 26
$\tau_0$ Relaxation attempt time, page 15
$\tau_B$ Brown relaxation time, page 19
$\tau_{B}^{\text{el}}$ Brown relaxation time for an ellipsoid, page 36
$\tau_D$ Total relaxation time, page 19
$\tau_N$ Néel relaxation time, page 15
$\tau_r$ Ellipsoid rotational relaxation time, page 36
$\tau_{\perp}$ Ellipsoid rotational relaxation time about the perpendicular axis, page 36
$\tau_{\parallel}$ Ellipsoid rotational relaxation time about the longitudinal axis, page 36
$\tau_B(\text{fit})$ Fitted $\tau_B$ from the fit of the rotational magnetic susceptibility, page 73
$\theta_{\text{an}}$ Angle of the anisotropy axis w.r.t. the easy axis, page 17
$T$ Temperature, page 4
$T_0$ Freezing Temperature, page 15
$t$ Time, page 22
$t'$ Time distinct from $t$, page 23
$t_{\text{sim}}$ Simulated time, page 41

$U$ Total potential energy, page 1

$U_{\text{LJ}}$ Lennard-Jones potential energy, page 31

$U_{\text{mag, int}}$ Internal magnetic potential energy between MNPs, page 32

$U_{\text{mag}}$ Magnetic energy, page 22

$U_{\text{tr}}$ Translational energy, page 22

$U_{\text{WCA}}$ WCA potential energy, page 31

$\mathbf{V}$ First rotation matrix for the SVD, page 44

$V$ Scalar from first rotation matrix for the SVD, page 43

$V_{\text{el}}$ Volume of an ellipsoid, page 36

$V_p$ Volume, page 2

$\mathbf{W}$ Final rotation matrix for the SVD, page 44

$W$ Scalar from final rotation matrix for the SVD, page 43

$X_{\text{ch}}$ Exchange, page 2

$\xi_{\text{rot}}$ Rotational stochastic component, page 23

$\xi_{\text{rot}}$ Scalar from rotational stochastic component, page 24

$\xi_{\text{tr}}$ Translational stochastic component, page 22

$\xi_{\text{tr}}$ Scalar from translational stochastic component, page 23
Acronyms

CGS centimetre-gram-second unit system. 2

DLVO Derjaguin-Landau-Verwey-Overbeek potential. 13, 100

FCC Face-centred cubic. 8

FT Fourier transform. 40

LLG Landau-Lifshitz-Gilbert equation. 20

LRT Linear response theory. 15, 16, 56

LSMO La$_{1-x}$Sr$_x$MnO$_3$. iii, vi, 6, 8–10, 20, 38, 68, 70, 91, 94, 96

LSMO$_{35}$ LSMO with a strontium fraction of $x = 0.35$. v, vii–ix, 9, 20, 38, 62–64, 69–76, 78, 81, 83, 85, 86, 91, 92, 94–96, 98, 99, 103–105

LSMO$_{40}$ LSMO with a strontium fraction of $x = 0.4$. v, viii, ix, 70, 72–74, 92, 94–96, 98, 99, 106

MACF Magnetic autocorrelation function. 39, 44, 67


PRNG Pseudo random number generator. 32, 33

RF Radio frequency. 5, 6, 8, 38

RMSD Root mean squared deviation. 43

SAR Specific absorption rate. iv, v, 5, 6, 8–12, 17, 19–21, 38, 70, 93–96, 99

sLLG Stochastic Landau-Lifshitz-Gilbert equation. 21, 25, 34, 68, 70

SVD Singular value decomposition. 43

WCA Weeks-Chandler-Anderson potential. 21, 31, 32, 48, 50, 68
Articles, Conference Presentations, and Software

- K. McBride et al. “Evaluation of La$_{1-x}$Sr$_x$MnO$_3$ ($0 \leq x < 0.4$) synthesised via a modified sol–gel method as mediators for magnetic fluid hyperthermia”. In: *CrystEngComm* 18.3 (2016), pp. 407–416. DOI: 10.1039/c5ce01890k


- Katherine McBride et al. “Improving the crystallinity and magnetocaloric effect of the perovskite La$_{0.65}$Sr$_{0.35}$MnO$_3$ using microwave irradiation”. In: *CrystEngComm* 19.27 (2017), pp. 3776–3791. DOI: 10.1039/c7ce00882a

- J. Cook et al. “Effect of aggregation on the radio-frequency heating of ferromagnetic manganite nanoparticles”. In: (Nanoscale Simulators of Ireland, Limerick). 2018

A magnet in a non-magnetic fluid that is placed in a magnetic field will experience a torque inducing the magnet to align with the field. The torque, $\mathbf{\tau}$, is the vector product of the magnetic moment, $\mathbf{m}$, of the magnet and the strength of the external magnetic field, $\mathbf{H}$, as seen in Eqn 1.1. In the case of an electron, the moment is due to its intrinsic spin (as with other fundamental particles) which has a value of $-9.28 \times 10^{-21} \text{erg G}^{-1}$.

$$\mathbf{\tau} = \mathbf{m} \times \mathbf{H}$$  \hspace{1cm} (1.1)

To minimise the energy of the system,

$$U = -\mathbf{m} \cdot \mathbf{H}$$  \hspace{1cm} (1.2)

the magnetic moment aligns with the direction of $\mathbf{H}$, but thermal fluctuations will prevent complete alignment at any finite temperature.

In non-magnetic materials, the sum of the local magnetic moments is zero, leading to no overall magnetisation. Paramagnetic materials are non-magnetic materials that have randomly orientated magnetic moments [1]. When placed in an applied magnetic field, these magnetic moments will align along the direction of the field inducing an overall magnetisation of,

$$M(\mathbf{H}) = \frac{N\mathbf{m}}{V_p} L \left( \frac{m_{\text{sat}}|\mathbf{H}|}{k_B T} \right)$$

where,

$$L(x) = \coth(x) - \frac{1}{x}$$  \hspace{1cm} (1.3)
and $m_{\text{sat}} = \frac{|m|}{V_p}$. Magnetisation is related to the magnetic field by the Langevin function, $L(x)$, as seen in Eqn 1.3, where $N$ is the number of particles, $V_p$ is the total volume of the ferromagnet and $k_B$ is the Boltzmann constant and $T$ is the temperature of the system [2]. The magnetisation is measured in $\text{emu/cm}^3$ as denoted by CGS units used throughout this work [3]. In ferromagnetic materials, the magnetic moments spontaneously align along one of the most energetically favourable crystalline directions known as easy axes.

A magnetic material is only ferromagnetic below a transition temperature known as the Curie temperature, $T_c$. For a ferromagnetic materials such as ferrite, the iron allotrope, the Curie temperatures are in excess of 500 K [4]. Above the Curie temperature the material will behave as a paramagnet. The Curie temperature is affected by properties of the material such as its crystal structure and the size of the sample [5].

These properties of magnetic particles apply to all magnetic materials but the situation gets complex when considering interacting magnetic moments. This is the particular challenge when attempting to calculate the overall magnetisation of a chain or cluster of magnetic nanoparticles (MNPs). By convention these particles are defined as ferromagnetic particles with radii below 100nm [6].

At low concentrations, the situation is relatively simple. The Langevin function as seen in Eqn 1.3, is valid for classical non-interacting magnetic moments in a uniform magnetic field e.g. single domain nanoparticles in a non-magnetic fluid [7], and the overall magnetisation, $M$, of the MNP is the simple vector addition of the particle magnetic moments.

However, at higher MNP concentrations the many-body interactions can have a large effect on the magnetisation of the system and cannot be neglected [8]. These interactions can take many forms. For instance, atomic magnetic moments of a material are not always aligned along the same direction. For particles above a critical radius,

$$r_c \approx 9 \frac{X_{\text{ch}}K_u^{1/2}}{m_{\text{sat}}^2}$$  \hspace{1cm} (1.4)

multiple domains are more energetically favourable than the complete alignment of the atomic magnetic moments of a material along a single direction [9]. A good estimate for the radii was first derived by Kittel given by Eqn 1.4 where $X_{\text{ch}}$ is the exchange, $K$ is the uniaxial anisotropy and $m_{\text{sat}}$ is the saturation magnetisation of the particle [9, 10].

Domain walls separate adjacent domains. Across a domain wall the direction of the magnetic moment rotates from the overall magnetisation of the first domain to the
second. For small nanoparticles (the exact size depends on the material) a single domain is more energetically favourable than multiple domains [9]. The size of single domain particles is dependant on the material of the particle, for instance ferrite is single domain when the radii less than 30nm [9, 11]. However single domain particles can have a radius of up to 1000nm [10].

In solution, all magnetic particles undergo Brown relaxation, the rigid rotation of the particle to align with the magnetic field [12]. There are two major factors that affect the Brown relaxation time. The first is the effect of many-body interactions such as occur with magnetic particles in solution [8]. The second is the shape of the magnetic particle. Brown relaxation is faster for spherical particles than for more abstract shapes such as ellipsoids [13].

Single domain magnetic particles are simpler to describe theoretically than particles with multiple domains due to the additional complexity associated with interactions across domain walls. A superparamagnetic particle is a single domain ferromagnet. In addition to Brownian relaxation, a superparamagnetic nanoparticle undergoes Néel relaxation. Néel relaxation is the internal rotation of the overall magnetic moment of the particle towards the most energetically favourable direction, i.e. an easy axis. The Néel relaxation time is the mean time between two spontaneous reversals of the direction of the magnetic moment between parallel and anti-parallel to its easy axis under thermal conditions [12].

Brownian and Néel relaxations to an easy axis are always accompanied by a loss of energy to the environment. At equilibrium, the dissipation of energy is compensated by the thermal fluctuations as described by the fluctuation-dissipation theorem (Section 3.3.2) [14].

The application of an external AC magnetic field,

\[ \mathbf{H} = H_0 \cos(\omega t) \]  

(1.5)

where \( H_0 \) is the external magnetic field strength at \( t = 0 \), induces both Brownian and Néel rotation in a MNP solution. During the process, some heat is generated. The heat generation is both dependent on the amplitude of the magnetic field as well as the frequency, \( \omega \) of the oscillating field. The response of a MNP in solution to an external AC field is given by,

\[ \chi_{\alpha\beta}(\omega) = \frac{\partial M_\alpha}{\partial H_\beta} \]  

(1.6)

known as the magnetic susceptibility where \( \alpha \) is the direction of the total magnetic moment of the nanoparticle and \( \beta \) is the direction of the external field. The heat dissipated, \( P \), is related to the imaginary part of the susceptibility as shown below [15,
The use of a magnetic field to generate heat in the region around a MNP is called magnetic hyperthermia. Magnetic hyperthermia can provide an alternative treatment to invasive cancer therapies such as radiotherapy and chemotherapy. Chemotherapy drugs affect the whole body, since they are injected into the blood stream to inhibit cell division and inducing apoptosis and inhibiting cell division in cancerous cells [17]. A side-effect of these drugs is that healthy cells are also affected as it is not a targeted treatment. The un-targeted drugs also inhibit the bodies immune system and is therefore more susceptible to other usually benign illnesses [17]. Radiotherapy is slightly less invasive because high energy radiation is targeted at a tumour location [17]. However, the radiation has to penetrate through healthy tissue to reach the tumour. In principle, magnetic hyperthermia gives more control as heat can be generated at a specific location minimising the damage to healthy cells. Modelling the heating of MNPs in biological fluids and tissues will help design better MNPs for a viable cancer treatment.

Heat transport in biological tissue is primarily through conductive mechanisms and is dependent on Fourier’s law as seen in Eqn 1.8 [18–20].

\[ q = -k\nabla T \]  

(1.8)

where the local heat flux density, \( q \) also known as the energy current, is proportional to the negative temperature gradient, \( -\nabla T \), through the material’s thermal conductivity, \( k \).

Mechanisms such as convection are negligible for nanometre scale systems. At such small scales the Reynolds number of the fluid will be very small so the flow will most likely be laminar. Convection is the smallest component in laminar systems as it is heat transfer by mixing. The Pennes transport equation,

\[ \rho c_p \frac{\partial T}{\partial t} = -\nabla q + Q_{so} + Q_{si} \]  

(1.9)

enables the calculation of the heat transfer around systems of MNPs [21, 22]. To solve Eqn 1.9, the finite element method is used which requires knowledge of the geometry of the system as well as properties such as the density (\( \rho \)) and the heat capacity (\( c_p \)) and where heat is absorbed (\( Q_{si} \)) or generated within the tissue (\( Q_{so} \)).

To have an effect on tissue the surrounding temperature of a human cell needs to be raised to greater than 314K where apoptosis (programmed cell death) starts to occur [23]. Well researched particles such as magnetites achieve a high enough temperature well within their Curie temperature. The risk of damaging healthy tissue at
such high temperatures should be avoided. Materials with a Curie temperature in the region of 314 K to 319 K such as La$_{1-x}$Sr$_x$MnO$_3$ would be more suited to use in vivo [23]. Toxicity of the nanoparticles must be also taken into account before considering any use in vivo.

In this work we will focus on heat sources and how MNP interactions affect the heat generation properties of the solution. We plan to model the magnetic response of MNPs in solution coupled with a dipole-dipole interaction. Assuming that short chains are the most common and basic state of magnetic aggregation, we focus on the investigation of their linear response. In particular we wish to determine to what extent the chain length and particle diameter affect the magnetic susceptibility of the solution and the resulting specific absorption rate (SAR), the radio frequency (RF) power absorbed per unit mass of an MNP. We have further discussed the aims of this work with a reflection on current research in Section 2.3.
Chapter 2

Background

In this chapter I will give an overview of the biological heating applications, along with the current state of the art simulations, of the RF response of magnetic nanoparticles. I will explain why biological heat transfer is an important area of research and examine the current methods of generating heat using MNPs. Specifically I will show why La$_{1-x}$Sr$_x$MnO$_3$ (LSMO) is a good candidate for biological heat generation. In this chapter I will review the properties that can be acquired from experiments with MNPs and this will help direct the development of numerical simulations of MNPs.

The eventual aim of this area of research is to develop MNPs with highly tuneable heat generation properties. The area I will focus on is the amount of heat generated by each MNP by examining the dynamics of individual MNPs, progressing to the dynamics of agglomerations of MNPs.

The value of note in MNP heat generation is the specific absorption rate (SAR) which is the RF power absorbed per unit mass of an MNP. The aim of this thesis is to be able to calculate this quantity from the simulations. At the end of this chapter I will describe the overall structure of the remaining part of my thesis.

2.1 Biological Heat Transfer using MNPs

The heating of biological matter is a useful method of inducing apoptosis (programmed cell death). If tissue is brought above $\sim 320 \text{K}$, cells start entering DNA repair routines leading to the eventual apoptosis of the cell [23, 24]. Moderate biological heating in the
range of 310 K to 320 K, known as mild hyperthermia, can lead to heat stress of cells [25, 26]. Dangers with external heating include the indiscriminate damage to healthy tissue. Unwanted damage is avoided with a precise approach to heat application. The motion of MNPs in solution, driven by an external alternating magnetic field, generates heat due to friction with the surrounding fluid [27]. To safely apply MNP heating in vivo, one needs to know how to control the amount of heat produced and where the heat is generated.

MNP movement in vivo has already been well researched, using both active mechanisms using external stimuli such as a magnetic field, and passive mechanisms such as shaped particles that are transported by the flow of the blood stream [28]. A review of particle movement by Bechinger et al. [28] suggests that the aim of future research should be directed towards more complex and crowded environments. More precisely the aim should be to engineer specific behaviours with biocompatible energy supplies to propel particles at sizes approaching nanometre scales. Our research aims to achieve this through gaining a greater insight into more complex MNP environments using alternating magnetic fields as the driving force to locally generate heat.

Not only do we need to consider heat generation, we also need to consider heat transfer continuing after the external AC magnetic field has been removed as the generated heat diffuses into the tissues. Improvements in heat transfer models in vivo enable the modelling of a source with a known energy [22, 29, 30].

A selective heat application method is needed so as to only cause the apoptosis of the tumoural cell and not of healthy cells [31]. Increases in the solvent temperature will change the magnetic susceptibility of the particles leading to changes in the amount of heat released to the system [32, 33].

2.1.1 The Curie temperature and selection of particle type for biological hyperthermic treatment

Magnetic particles will stop responding to an external magnetic field above the Curie temperature. Curie temperatures for Magnetite and similar metal oxide MNPs are greater than 500 K [4]. Magnetite nanomaterials are biologically compatible and have been widely studied both theoretically and experimentally [34–36]. As Demortière et al. [36] show it is possible to create magnetite MNPs with a narrow size distribution with a standard deviation of less than 20% of MNPs within the 2 nm to 14 nm range.

The control of magnetic heating provided by the Curie temperature of magnetite nanoparticles is well outside the temperatures of biological hyperthermic treatment. We therefore need another material if we are going to use the Curie temperature to
limit treatment. Perovskite MNPs such as LSMO have an advantage over other magnetite MNPs by having a Curie temperature that can be adjusted within the lower range of cell apoptosis [37, 38]. Perovskites are defined by their crystal structure which is a face-centred cubic (FCC) lattice with the configuration ABO₃, originating from the material perovskite which was the first material discovered with the structure. The perovskite structure, ABO₃, can be distorted by the introduction of dopant at cite A as seen in Fig. 2.1.

![Figure 2.1: Structure of perovskites of the type ABO₃. a) shows the undoped compound LaMnO₃ and b) shows the distortion caused to the lattice with dopant in La₁₋ₓSrₓMnO₃ compounds [26]. The black (darkgreen) dots show the dopant, strontium.](image)

With LSMO the crystal distortion caused by the strontium dopant changes magnetic characteristics of the material such as its Curie temperature [26]. For instance, with a strontium fraction of x = 0.25, the Curie temperature of LSMO is 346 K whereas with a strontium fraction of x = 0.35 the Curie temperature is 362 K [23]. The phase diagram of LSMO below (Fig. 2.2) shows a strontium fraction of x = 0.3 is the compound with the highest Curie temperature. Although the Curie temperature is above the mild hyperthermia range, the maximum temperature achieved by the RF heating of particles in water is 320 K [26]. Above the Curie temperature of an immobilised MNP the SAR is zero, acting as a natural safety mechanism for mild hyperthermic treatment, due to the MNP no longer responding to an applied magnetic field [39].

Changing the amount of strontium dopant in LSMO is shown to modify the magnetic saturation value which is due to the varying distortions of the crystal structure of the material [26]. The magnetic saturation value for a dopant of x = 0.25 is 12 800 emu mol⁻¹ increasing slightly to 13 000 emu mol⁻¹ for a dopant of x = 0.35 before dropping off sharply to 3500 emu mol⁻¹ for a dopant of x = 0.4. The changing of
2.1. Biological Heat Transfer using MNPs

The magnetic saturation of the MNP is a main magnetic quantity that will change the eventual SAR of the material. The SAR of the MNP is also dependent on the shape of the MNP.

2.1.2 Synthesis Methods for LSMO nanoparticles

Synthesis methods to create the particles greatly affects the SAR and therefore the maximum temperature achieved within an AC magnetic field. The maximum temperature that can be achieved increases by 42.3 K when the sol-gel method is assisted with microwave radiation for LSMO with a strontium fraction of $x = 0.35$ (LSMO35) [23, 40]. The sol-gel method to create LSMO uses a solution of precursors La$_2$O$_3$, MnCO$_3$ and SrCO$_3$, in the desired ratios, suspended in water. The reaction to form LSMO occurs in the water before allowing the solution to dry out, a process known as sintering. Increasing the final sintering temperature used to create LSMO from 873 K to 1273 K increases the size of individual particles from 37 nm to 163 nm whilst increasing the Curie temperature from 311 K to 330 K [26, 41].

Other synthesis processes include reactive ball milling, solution combustion and copre-
2.1. Biological Heat Transfer using MNPs

cipitation, each of which create different properties such as the amount of agglomeration and particle size control [42, 43]. Along with the Curie temperature of MNPs, other magnetic properties are affected by the synthesis process, these include the magnetic saturation and susceptibility which in turn changes the SAR for the particle [44–46]. The higher the magnetic susceptibility of the particle the more energy can be released by particle movement therefore increasing the SAR.

For LSMO, reactive ball milling uses the same precursors as the sol-gel method but the reaction occurs using percussive means before sintering [42]. Manh et al. [42] show that a narrow size distribution of MNP can be achieved and they go on to suggest that increasing MNP size increases the SAR of the MNP due to less internal strain caused by larger magnetic domains. A larger crystalline structure can lead to a more magnetically aligned sample allowing for a higher magnetic saturation and therefore a larger SAR.

Some perovskite structures such as La$_{1-x}$Ba$_x$MnO$_3$ or La$_{0.7}$Sr$_{0.3}$Mn$_{1-x}$M$'_x$O$_3$ ($M'=$Al,Ti) cool the solution when exposed to an AC magnetic field and could be used for finer control of the temperature of the MNP [47, 48]. Coatings for magnetite and perovskites in biocompatible materials like dextran sulphate leads to high compatibility with the host leading to a wider array of targets accessible to the MNPs [49, 50]. Clustering of particles is promoted by use of hydrothermal synthesis methods over coprecipitation methods which is less desirable in biological applications as the SAR of the MNPs is reduced [51].

Controls on heat generation from MNPs is affected by various properties of the system such as the dispersion of the nanoparticles within the system and the viscosity of the solvent [52]. MNPs within a cluster can rotate individually and as a whole cluster leading to more heat generation options [53, 54]. Measurements of the SAR of MNPs in physical experiments often differ from theoretical simulations. The difficulties in obtaining accurate measurements is because of uncontrolled errors such as heat generation from equipment [55–57].

Experiments exploring the heat generation of MNPs are commonly carried out using the method described by McBride et al. [23, 26]. The experiment is setup as shown in Fig. 2.3. After the MNPs are produced they are suspended in solution, which in the case of McBride et al. is water. The MNP solution test tube is surrounded with polystyrene to reduce radiative heating from the electromagnetic coil.
The temperature dependence of the SAR and the effect of MNP concentration on the amount of heat generated adds more uncertainty to the measurements [58, 59]. As Périgo et al. [58] show the SAR of MNPs is linearly dependent on the MNP temperature for MNPs greater than 24 nm in diameter while the solution temperature is below the MNPs Curie temperature. Tailoring the SAR of the MNPs is needed to improve the efficiency of magnetic hyperthermia keeping external magnetic fields below biologically safe limits [60, 61].

The SAR of different MNPs is shown in table 2.1 below. It reveals that there can be substantial variations in SAR depending on the size of the nanoparticles as well as the chemical composition. Iron based nanoparticles are on the whole smaller than lanthanum based nanoparticles due to both the wealth of research into the former as well as chemical and mechanical properties. It is also interesting to note that [37] claim a much higher accuracy (uncertainty of +/- 2) compared to [42]. It is unclear whether this is due to better experimental methodology, smaller errors with larger MNPs, or unrealistic error estimates.

Figure 2.3: Schematic of equipment used for heating experiments by McBride et al. [26].
### 2.2 Models of MNPs and their properties

The range in experimental estimates of SAR and its dependence on size and temperature highlights the need for improved quantitative knowledge of the fundamental processes. One approach to this is the development of models to represent the interactions. To be able to model the SAR of MNPs, knowledge of the intraparticle and interparticle dynamics of MNPs is needed. As Deatsch et al. show, understanding aggregation and agglomeration is the main challenge to completely understanding the dynamics of MNPs [62]. Theoretical monodispersion dynamics are however understood to a much greater degree [63]. The agglomeration of particles is hard to model at a macroscopic level due to the computational resources required to resolve macroscopic and microscopic phenomena. To be able to model at a macroscopic level efficiently microscopic properties of the model need to be approximated. The connection between macroscopic and microscopic phenomena usually involves simplifying of the model. The simplification of a model can produce an invalid model that does not reflect reality. It is therefore often not possible to compare aggregation affects with experimental studies.

<table>
<thead>
<tr>
<th>Type</th>
<th>Diameter nm</th>
<th>SAR W g⁻¹</th>
<th>Ms emu g⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₃O₄[36]</td>
<td>14</td>
<td>78</td>
<td></td>
</tr>
<tr>
<td>Fe₃O₄[45]</td>
<td>25</td>
<td>120</td>
<td>80</td>
</tr>
<tr>
<td>Fe₃O₄[32]</td>
<td>6.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe₃O₄[50]</td>
<td>35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe₃O₄[46]</td>
<td>10</td>
<td>65</td>
<td></td>
</tr>
<tr>
<td>Y₃Fe₅O₁₂[46]</td>
<td>50</td>
<td>22</td>
<td></td>
</tr>
<tr>
<td>MnFe₂O₄[60]</td>
<td>11.3</td>
<td></td>
<td>293</td>
</tr>
<tr>
<td>Mn0.75Zn0.25Fe₂O₄[60]</td>
<td>11.1</td>
<td></td>
<td>302</td>
</tr>
<tr>
<td>Mn0.75Co0.25Fe₂O₄[60]</td>
<td>11.4</td>
<td></td>
<td>309</td>
</tr>
<tr>
<td>CoFe₂O₄[60]</td>
<td>9.1</td>
<td></td>
<td>272</td>
</tr>
<tr>
<td>La₀.78Sr₀.22MnO₃[43]</td>
<td>30±15</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>La₀.7Sr₀.3MnO₃[42]</td>
<td>20</td>
<td>10–26</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>10–28</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>20–36</td>
<td>54</td>
</tr>
<tr>
<td>La₀.7Sr₀.3MnO₃[37]</td>
<td>85</td>
<td>80±2</td>
<td>63.27</td>
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<td>70</td>
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<td>36.45</td>
</tr>
<tr>
<td></td>
<td>170</td>
<td>80±2</td>
<td>32.53</td>
</tr>
<tr>
<td>La₀.75Sr₀.25MnO₃[26]</td>
<td>82</td>
<td>25–48</td>
<td>48</td>
</tr>
<tr>
<td>La₀.65Sr₀.35MnO₃[26]</td>
<td>82</td>
<td>45–60</td>
<td>49</td>
</tr>
<tr>
<td>La₀.6Sr₀.4MnO₃[26]</td>
<td>61</td>
<td>35–50</td>
<td>13</td>
</tr>
</tbody>
</table>

#### Table 2.1: MNP properties
because the effects are negligible at the length and time scales commonly explored in experimental studies.

2.2.1 Interparticle and intraparticle MNP dynamics

The interparticle dynamics of MNPs have been extensively simulated using Langevin dynamics for complex structures of MNPs [64–66]. The aim of Langevin dynamics is to simulate a system of particles without explicitly modelling the environment. Langevin dynamics is specifically an extension to molecular dynamics where the surroundings are modelled using a thermostat and the viscosity of the solvent surrounding the particles. By minimising the degrees of freedom in the system it is possible to model dynamics that happen over larger time periods due to the reduced computational complexity. However if variables are ignored that have a large effect on the particles the simulation can be unphysical.

Recent simulations by Osaci et al. show that the use of the combination of Langevin dynamics, for the rotation of MNPs, the Derjaguin-Landau-Verwey-Overbeek (DLVO) for translational potentials, combined with the Verlet algorithms can successfully simulate colloidal systems [67]. Osaci shows that when left in colloidal suspensions, MNPs tend to agglomerate dependant on the local surroundings, taking into account the proximity of other MNPs and interparticle forces within the system. Agglomerations of MNPs, sometimes known as clusters, are complex structures of particles held together by the interparticle forces between them. The simplest form of agglomeration is a two particle chain.

The formation of chains of magnetic nanoparticles is a spontaneous process in solutions of MNPs. A chain of MNPs is at the simplest form two MNPs held together with the magnetic interaction between them. Simple chains and more complicated network structures such as Y-junctions and rings can occur [68, 69]. As the chain length increases, rings are observed forming in both numerical and physical experiments [70]. Rings and chains can coexist in solution creating complex dynamics [64].

MNPs embedded in polymers connected with ‘polymer’ potentials are known as filaments [71]. Magnetic filaments and chains have a stronger magnetic response than standard ferrofluids. The stronger the external magnetic field, the stiffer both filaments and chains of magnetic nanoparticles become, this leads to up to a two fold increase magnetic susceptibility [71]. The magnetic susceptibility of the particle chains increases with longer chains in dilute systems due to the increase in volume of the MNPs [72]. As the solution of MNPs becomes more concentrated the increase is counteracted by larger interparticle forces which cause the chains to disintegrate [72, 73].
2.2. Models of MNPs and their properties

The Brown relaxation of a single spherical MNP and a prolate ellipsoidal MNP are known analytically (see Section 3.3.1.1) [13]. A prolate ellipsoid can be thought of as an approximation of a stiff chain of MNPs, equally an ellipsoid with the elongated axis infinitely extended, is an approximation of a wire [13]. If the relaxation of a chain of MNPs can be extrapolated from these two solutions it would reduce the complexity of future models. However knowing at what point the approximation should be disregarded would also be useful for further simulations. The approximation will inform whether chains of MNPs have the same dynamics as a single ellipsoid providing the opportunity to simplify models of MNPs [74]. Chains of magnetic particles have been described in physical experiments where fractal clusters are prevalent, particularly in biological applications, leading to the need for a complete picture of chain dynamics in simulations [75, 76].

Interactions between MNPs affect the dynamics of the agglomeration of particles. Modelling the magnetic interaction of magnetic nanoparticle chains can be split into three distinct regimes, interparticle interactions of the chain, rigid rotational interactions of the chain, and translational interactions. To model each interaction type, different methods are needed. In fixed lattice models MNP translational degrees of freedom are neglected completely [77]. In free models translations are commonly modelled using the Langevin equation as described in Section 3.1.

2.2.2 Néel Relaxation

The three main theoretical approaches used to include intraparticle dynamics in model systems of MNPs are mean field theory, linear response theory and Stoner-Wolfarth models [78].

2.2.2.1 Mean field theory

Interparticle dynamics can also be modelled using a combination of mean field theory and the finite element method. Mean field theory is an effective single particle model in which the external field is computed self-consistently, ignoring the fluctuations of the field. This is achieved in its simplest form by using methods like Euler’s method or the implicit midpoint method to minimise the change in the magnitude on the magnetic moment of an MNP (the latter is used in Section 3.2). The aim of mean field theory is to convert a many-body problem to a single-body problem by approximating a pertinent quantity, such as the magnetisation of each MNP, to a single averaged value.

This model allows for the splitting of the system into regions where it is assumed that
the magnetisation is uniform [79, 80]. Therefore translational Brownian relaxations are neglected and only the effect of Néel relaxation (the internal rotational relaxation) and rotational Brown dynamics (the rigid body rotational relaxations) are examined by the model [81, 82]. Correlations between particle positions and magnetic moment orientations are not accounted for [83]. If the assumption is valid at a specific region size, larger systems can be simulated without an increase in computational difficulty because the model can be simplified by having a uniform magnetic field. Finite element methods split a simulation region into sections where the mean field theory is applied in order to simulate bulk dynamics of a system of MNPs.

2.2.2.2 Linear response theory

Linear response theory (LRT) neglects external magnetic field interactions and is therefore the simplest model. By neglecting the external magnetic field, only Néel relaxation in LRT includes the effect of the anisotropy of the particle, ignoring possible magnetisation reversals due to a changing external field. The simplest form of magnetic anisotropy is uniaxial, each MNP has one preferential magnetisation axis known as the particles easy axis. LRT is only valid for MNPs where \( m_{sat} V H_{\text{max}} / k_B T < 1 \) where \( H_{\text{max}} \) is the maximum applied field [84]. Using this inequality, it can be shown that LRT is good at reproducing experimentally determined results for \( \text{La}_{1-x}\text{Sr}_x\text{MnO}_3 \) for MNPs of around 40 nm diameter where the strontium fraction is in the \( 0.15 \leq x \leq 0.45 \) range [85].

Néel relaxations are modelled using the anisotropy energy within an energy barrier type model, comparable to the Arrhenius law [86]. In the case of MNPs, the energy barrier is the energy required to align with the easy axis.

\[
\tau_N = \tau_0 \exp \left( \frac{E_{\text{an}}}{k_B T} \right)
\]

(2.1)

where \( E_{\text{an}} \) is the anisotropy energy of the MNP, \( \tau_N \) is the Néel relaxation time and \( \tau_0 \) is the relaxation attempt time (~\( 10^{-9} \) s) [86]. Models of Néel relaxations are only applicable when a particle is small as complete relaxations only occur below a particle diameter of a few 100 nm [87].

For small nanoparticles below 18 nm in radius, Néel relaxations are the dominant relaxation process [88, 89]. The Vogel-Fulcher model, [90], modifies Eqn 2.1, allowing for the fitting of the temperature dependence of \( \tau_N \) by

\[
\tau_N = \tau_0 \exp \left( \frac{E_{\text{an}}}{k_B (T - T_0)} \right)
\]

(2.2)

where \( T_0 \) is a measure of the particle-particle interaction effect, otherwise known as the
freezing temperature (Eqn 2.7) [86, 90, 91]. The freezing temperature is the temperature below which the orientation of the MNP’s magnetic moment is ‘frozen’ [92]. The magnetic anisotropy of MNPs is not constant at all temperature ranges therefore it is important to take into account the system temperature [93]. For LRT the anisotropy energy is defined as

$$\begin{align*}
E_{\text{an}}^{\ell r} &= K_a V_p
\end{align*}$$

(2.3)

It is assumed in LRT that the easy axis of the particle is aligned with the magnetic moment of the MNP. Therefore in LRT a Néel relaxation reverses the polarity of the magnetic moment of a MNP. Extensions to LRT, such as the Stoner-Walfarth model, add the more complex situation of having an angle between the easy axis of the MNP and the magnetic moment.

2.2.2.3 Stoner-Walfarth model

The Stoner-Walfarth model can be used to simply approximate the magnetic hysteresis of a system of MNPs. A magnetic hysteresis curve shows the change in the magnetisation of a particle as an applied field reverses magnetisation direction, but is only applicable for particles with uniaxial easy axes [39, 94].

Single domain MNPs experiments are well modelled by the Stoner-Walfarth model but for more complex systems the model can be modified to describe physical experiments of MNPs more accurately [95]. Chains of MNPs have a tendency to be uniaxial leading to a good agreement with physical experiments [96]. In a stable chain the magnetic moment of each particle is aligned along the chain. The anisotropy of the chain is more likely to be uniaxial as the magnetic interaction with surrounding MNPs makes the chain axis an easier axis. Modifications to the Stoner-Walfarth models can examine more complex systems with the inclusion of more accurate anisotropy energy models [86].

Furthermore, the magnetic anisotropy of individual particles within a chain has a large impact on the internal dynamics of each MNP. For complex crystal structures there are many more easy axes, for instance $\gamma$–Fe$_2$O$_3$ has 3 easy axes (i.e. cubic anisotropy) [1]. Single domain ferromagnets are most commonly uniaxial, triaxial or cubic [1]. The cubic anisotropy energy is defined as

$$\begin{align*}
E_{\text{an}}^{\text{cub}} &= KV_p(A^2B^2 + B^2C^2 + C^2A^2)
\end{align*}$$

(2.4)

where $A, B, C$ are directional cosines of the magnetic moment of the ferromagnet with respect to the easy axis of the particle where $A^2 + B^2 + C^2 = 1$ and $K$ is the anisotropy factor.
Cubic anisotropy ferromagnets have four easy axes if the anisotropy constant of the particle, $K < 0$ otherwise there are three axes. Triaxial ferromagnets have an easy, intermediate and hard axis. The hard axis is the axis with the highest magnetic anisotropy energy and the intermediate axis is a saddle point in the free energy surface. For triaxial ferromagnets the anisotropy energy reduces to

$$E_{\text{tri}} = K_a V_p A^2 + K_b V_p B^2$$

(2.5)

where $K_a$ and $K_b$ are the triaxial anisotropic factors of the particle. For uniaxial anisotropy we only consider a single axis so Eqn 2.4 reduces to [78, 97]

$$E_{\text{uni}} = K_u V_p (1 - C^2) = K_u V_p \sin^2 \theta_{an}$$

(2.6)

where $K_u$ is the uniaxial anisotropic factor of the particle, $V_p$ is the volume and $\theta$ is the angle of the anisotropy axis w.r.t. the easy axis.

The magnetic anisotropy of a particle changes the shape of the associated hysteresis curve as Fig. 2.4 shows [98, 99].

![Anisotropy axes](image)

**Figure 2.4:** Hysteresis loops for magnetite MNPs with 1 - 4 anisotropy axes [99]. $m(t)$ is the normalised MNP magnetisation and $h(t)$ is the normalised applied magnetic field, normalised to the maximum applied magnetic field.

If a single domain ferromagnet has no anisotropy the particle is superparamagnetic and the hysteresis curve has no internal area i.e. the magnetisation and demagnetisation of the particle follows the same trend [100]. Above the material’s Curie temperature the hysteresis loop can have no area, and as the SAR is proportional to the areas enclosed by the hysteresis loop for immobilised particles the SAR is zero [39].
Modifications made to Eqns 2.1 and 2.2 are used in models of rotational magnetic relaxation of particles such as the mean-field theory and the Stoner-Walfarth model. The total anisotropy energy for a ‘Stoner particle’ (a particle where all magnetic moments within the particle are aligned in the same direction) includes the potential energy of the MNP in an external field, known as the Zeeman energy [39, 86, 101].

\[ E_{sw}^{an} = E_{an}^{uni} - m_{sat} H \cos(\theta_{an} - \phi_{an}) \]  

(2.7)

where \( \phi_{an} \) is the angle of the anisotropy axis w.r.t. the external magnetic field axis as shown below in Fig. 2.5 [102].

![Figure 2.5: The Stoner-Walfarth model of anisotropy for a spherical MNP. The red dotted line is the anisotropy axis of the MNP.](image)

The method allows variation of the magnetic moment along a single plane and is valid for single domain ferromagnets where \( \kappa < 0.7 \) where [78]

\[ \kappa = \frac{k_B T}{K_{eff} V_p} \ln \left( \frac{k_B T}{4m_{sat} H_{max} V_p^2 F_0} \right), \]  

(2.8)

where \( K_{eff} \) is the effective anisotropy of the MNP and \( H_{max} \) is the maximum applied magnetic field strength. The dimensionless parameter \( \kappa \) shows the variation in the ability of an MNP to resist an external magnetic field without undergoing demagnetisation, known as the coercive field. For immobilised particles once \( \kappa > 1.6 \) the hysteresis loop is reversible therefore there is no hysteresis losses and the particles are no use for magnetic hyperthermia. The particles are of no use because the coercive field, the measure of the resistance to demagnetisation of MNP’s, is almost zero [78, 103].
2.2. Models of MNPs and their properties

2.2.3 Brownian Relaxation

Rotational Brownian relaxation is an important addition when modelling MNPs in a fluid where the particles are free to rotate in space [40]. Calculating the total relaxation time, $\tau_D$, of a particle is achieved by [78, 104]

$$\frac{1}{\tau_D} = \frac{1}{\tau_N} + \frac{1}{\tau_B}$$

(2.9)

where $\tau_B$ the Brown relaxation time is given by [105]

$$\tau_B = \frac{3\eta V}{k_B T}$$

(2.10)

where $\eta$ is the dynamic viscosity of the solvent. For water, $\eta = 1.002 \times 10^{-2}$ g cm$^{-1}$ s$^{-1}$ and human blood has an average viscosity of $\eta = 3 - 4$ g cm$^{-1}$ s$^{-1}$ [106, 107]. The Brown relaxation time is increased by the shape anisotropy of MNPs because of the increase in hydrodynamic volume for non-spherical MNPs with equal volume to their spherical counterparts [108].

Brown becomes the dominant process over Néel relaxation as the particle diameter becomes larger than 15 nm [109]. A 24 nm radius spherical magnetite nanoparticles $\tau_N$ is around $10^8$ s and $\tau_B$ is around $10^{-5}$ s but for 14 nm radius $\tau_N$ reduces to around $10^{-2}$ s and $\tau_B$ is of the same order of magnitude [58]. Cubic particles will display a larger SAR compared to a spherical particle due to the shape anisotropy of the MNP [108]. The SAR is further increased by increasing the viscosity of the fluid the MNP’s are suspended in [110], although in biological media the solvent is not modifiable.

Most research so far has neglected all rigid body rotation and translational effects only modelling the internal dynamics described here. It is assumed that the neglected dynamics of MNPs in vivo are immaterial because the majority of MNPs are immobilised within the biological media although this is not always the case. Therefore any magnetic field will only induce internal rotation unless the MNP is in solution. Physical experiments on MNPs are usually carried out in solution, especially for large MNP experiments [26]. The interpretation of any results from experiments in solution requires examination of the rigid body translations and rotations of the MNPs, and the effect of agglomeration of MNPs on the dynamics of the system. The neglected dynamics are only needed when the MNPs are in solution.
2.3 Structure of Thesis

The review has shown that existing methods of calculating SAR for clusters and chains of MNPs have severe limitations. In order to examine both the particle positions and magnetic moment orientations of MNPs with time along with the ability to model basic Néel relaxation of MNPs we have chosen to develop a model using Langevin dynamics in combination with Linear response theory. We aim to model agglomerations of MNPs and investigate how the clustering effects the SAR of the MNPs. The Landau-Lifshitz equation or variations on the Landau-Lifshitz equation such as the Landau-Lifshitz-Gilbert (LLG) equation. The LLG improves the reproduction of experimental setups with high damping conditions in simulations and are used widely to model Néel rotations within MNP systems [111, 112]. The LLG can also be used to model all types of magnetic interaction between MNPs in high friction solutions (see Section 3.1).

The overall aim of our model is to be able to model the individual dynamics of MNPs including individual magnetic moments, the combination of which was not available in programs found at the beginning of this project. By modelling MNPs we hope to be able to extract information on the heat generation properties of MNPs in solution. The use of the LLG will give us the ability to include the effects of rotational and translation interactions via collisions or magnetic interactions because of the relatively light computational load needed to compute the LLG for MNPs. The eventual aim of the model is to provide experimentalists with a way of estimating the specific absorption rate of specific MNPs without having to synthesise and test them. Therefore we hope to reduce the time it takes to test viable magnetic hyperthermia candidates.

In Chapter 3, we discuss the methodology we follow to calculate the SAR for these LSMO MNPs. We show how to calculate the magnetic density of states (MDOS) from a simulation and how it relates to the SAR. In Chapter 4, we describe the program design and simple usage of the code. In Chapter 5, we show results for the magnetic susceptibility and MDOS for MNPs of LSMO35. We will show calculated values for the SAR for LSMO35 and highlight the change when the strontium dopant is changed from $x = 0.35$ to $x = 0.4$. The work concludes with a discussion of the implications of this work for specific absorption rate and heating capabilities of these chains of MNPs.
Chapter 3

Methods

This chapter has been organised into 3 sections. In Section 3.1 we introduce the equations describing the motion of magnetic particles in solution. We explain how the stochastic Landau-Lifshitz-Gilbert (sLLG) can be used for both the translational and rotational magnetic potential in the strong friction limit. In Section 3.2 we go into detail about the numerical implementation of the equations of motion used to simulate the dynamics of magnetic nanoparticles in the model. We show our generalisation of the standard position Verlet and explain why we use the Weeks-Chandler-Anderson (WCA) for our translational potential.

Finally in Section 3.3 we describe the linear response of magnetic nanoparticles alongside the implementation of the response processing. Within the linear response we show how we calculate the magnetic susceptibility of MNPs along with the specific absorption rate. We also show how it is possible to decompose the magnetic susceptibility into two components, one for rigid magnetic dynamics of MNP chains and one for the interparticle dynamics of the MNPs.

3.1 The Equations of Motion

In this section we consider first the translational motion of MNPs, followed by their rotational motion. In both cases there is a stochastic component to the motion of the MNPs included in the definition of the forces for translational motion, and the torque for rotational motion of the MNP. The stochastic components are designed to model the influence of the environment on the system, without including all the degrees of freedom.
3.1. The Equations of Motion

of the environment. Such a stochastic process is usually referred to as ‘white noise’. Brownian motion of any particle is the collision with surrounding particles that are uncorrelated and independent from each other. An accurate, yet scalable, description of the system-environment interaction is obtained by modelling the environment in this way.

3.1.1 Translational Brownian Motion

The translational motion of a single Brownian particle in solution is described by the Langevin equation [67, 113].

\[
m_{\text{NP}} \frac{d^2 r_i}{dt^2} = f_i - \Gamma_{\text{tr}} \frac{dr_i}{dt} + \xi_{\text{tr},i}(t),
\]

where \( m_{\text{NP}} \) is the mass of the MNP, \( r_i \) is the position of the \( i^{\text{th}} \) MNP, \( f_i \) is the total conservative force, \( \xi_{\text{tr}} \) is the friction coefficient (see Eqn 3.5) and \( \xi_{\text{tr},i} \) is the translational stochastic component (see Eqn 3.6). The total force on a magnetic particle is defined by

\[
f_i = -\nabla_{r_i} U(m, r),
\]

where \( U(m, r) \) is the total energy, defined as

\[
U(m, r) = U_{\text{tr}}(r) + U_{\text{mag}}(m, r),
\]

The total energy due to the translational motion of the MNPs, \( U_{\text{tr}} \) is further discussed in Section 3.2.2. For a magnetic particle, the magnetic total energy, \( U_{\text{mag}} \), depend on both the MNP’s centre of mass position, \( r \) and magnetic moment, \( m \). In the case of pure dipole-dipole interaction, we have that

\[
U_{\text{mag}}(m, r) = -\sum_{i<j} \frac{1}{\hat{r}_{ij}} \left[ 3(m_i \cdot \hat{r}_{ij})(m_j \cdot \hat{r}_{ij}) - m_i \cdot m_j \right] - M \cdot H_{\text{ext}},
\]

where \( \hat{r}_{ij} \) is the Euclidean distance between particles \( i \) and \( j \), \( \hat{r}_{ij} \) is the magnitude of that distance, \( M = \sum_i m_i \) is the total magnetisation, and \( H_{\text{ext}} \) is an external magnetic field. Note that the field acts equally on all the MNPs.
3.1. The Equations of Motion

The friction coefficient, $\Gamma_{tr}$, is given by Stokes-Einstein law for a spherical particle [114].

$$\Gamma_{tr} = 3\pi \eta d ,$$  (3.5)

where $\eta$ is the viscosity of the solvent (e.g., water) and $d$ is the diameter of the spherical particle. The stochastic component of the force, $\xi_{tr,\alpha}(t)$, with $\alpha = x, y, z$ ($\beta$ is the coordinates of the component at time $t'$), is modelled by Gaussian stochastic processes with a zero average, $\langle \xi_{tr,\alpha}(t) \rangle = 0$, and $\delta$-correlated in time [115, 116]

$$\langle \xi_{tr,\alpha}(t) \xi_{tr,\beta}(t') \rangle = 2\Gamma_{tr} k_B T \delta_{ij} \delta_{\alpha\beta} \delta(t - t')$$  (3.6)

The magnitude of the collisions due to the Brownian motion of particles has a Gaussian distribution leading to the natural choice of ‘white noise’ for the stochastic process of MNPs [116]. The linear relationship between the time-correlation, $\langle \xi_{tr,\alpha}(t) \xi_{tr,\beta}(t') \rangle$ and the friction coefficient $\Gamma_{tr}$ is imposed by the fluctuation-dissipation theorem (Section 3.3.2). In this way the Langevin equation is guaranteed to relax to the expected equilibrium distribution for the translational degrees of freedom of the MNPs.

3.1.2 Rotational Brownian Motion

The rotation of the magnetic moment of each particle is governed by rotational Langevin dynamics [67, 112, 117]

$$\frac{dn_i}{dt} = \omega_i \times n_i ,$$  (3.7)

$$I \frac{d\omega_i}{dt} = (m_i \times H_{\text{tot},i}) - \Gamma_{\text{rot}}\omega_i + \xi_{\text{rot},i}(t) ,$$  (3.8)

where $n_i$ is the anisotropy axis of the $i^{th}$ MNP (in our case we assume this is aligned with $m_i$), $\omega_i$ is the angular velocity of the $i^{th}$ MNP, $\Gamma_{\text{rot}}$ is the rotational friction
3.1. The Equations of Motion

coefficient (see Eqn 3.12), $\xi_{\text{rot}}$ is the rotational stochastic component (see Eqn 3.13) and [117]

$$I = \frac{1}{10} m_{\text{NP}} d^2$$

(3.9)

is the moment of inertia of a solid sphere of mass $m_{\text{NP}}$ and diameter $d$. The corresponding tensor of inertia, $I$, is given by $I = I \mathbf{1}$, where $\mathbf{1}$ is the three-dimensional unit matrix. The total (both inter particle and external) magnetic field ($H_{\text{tot},i}$) acting on the $i^{th}$ MNP, is given by

$$H_{\text{tot},i} = -\nabla_m U_{\text{mag}}(m, r)$$

(3.10)

where the potential energy is defined in Eqn 3.4. In the case of a pure dipole-dipole interaction we have that

$$H_{\text{tot},i} = \sum_{j \neq i} \frac{1}{r_{ij}^3} [3(m_j \cdot \hat{r}_{ij})\hat{r}_{ij} - m_j] + H_{\text{ext}}$$

(3.11)

The rotational friction coefficient, $\Gamma_{\text{rot}}$, is given by Faxen-Einstein law [114].

$$\Gamma_{\text{rot}} = \pi \eta d^3$$

(3.12)

As with the translational case, the thermal fluctuations are modelled by Gaussian stochastic processes, $\xi_{\text{rot},i\alpha}(t)$, with zero average and $\delta$-correlated in time:

$$\langle \xi_{\text{rot},i\alpha}(t)\xi_{\text{rot},i\beta}(t') \rangle = 2\Gamma_{\text{rot}} k_B T \delta_{ij} \delta_{\alpha\beta} \delta(t - t')$$

(3.13)

Due to the small size of the MNPs and in the absence of strong convection in the solution, we can take the low Reynolds number limit and neglect the rotational inertia setting $I \frac{d\omega_i}{dt} = 0$. In the following, we will also assume that the magnetic moment, $m_i$, of the MNP is either parallel or anti-parallel to the anisotropy axis, $n_i$. This is a reliable assumption if the internal magnetic (or Néel) relaxation can be neglected, i.e., for MNP larger than 100 nm [87].

By solving Eqn 3.8 for $\omega_i$ in the low Reynold number limit, substituting into Eqn 3.7, and using that $m_i \propto n_i$, we obtain that the Langevin equation for the rotational Brownian motion

$$\frac{dm_i}{dt} = -\frac{1}{\Gamma_{\text{rot}}} m_i \times [(m_i \times H_{\text{tot},i}) + \xi_{\text{rot},i}(t)]$$

(3.14)

It is worth noting that Eqn 3.14 can be also be obtained in the strong friction limit

3.2. Implementation

\((\alpha \to -\infty)\) of the sLLG equation \([118, 119]\)

\[
\frac{d\mathbf{m}_i}{dt} = \frac{\gamma_0}{1 + \alpha^2} \mathbf{m}_i \times \left( \mathbf{H}_{\text{tot},i} + \mathbf{H}_{\text{th},i} \right) + \frac{\alpha}{|\mathbf{m}_i|} \mathbf{m}_i \times \left( \mathbf{H}_{\text{tot},i} + \mathbf{H}_{\text{th},i} \right),
\]

(3.15)

where \(\gamma_0\) is the bare gyromagnetic ratio of the electron \((-17.61 \text{ G}^{-1}\text{ps}^{-1})\) and

\[
\mathbf{H}_{\text{th},i} = \sqrt{\frac{2\alpha k_B T}{\gamma_0|\mathbf{m}_i|}} \xi_{\text{rot},i},
\]

(3.16)

accounts for the thermal fluctuation of the magnetic field. In particular, Eqn 3.15 and Eqn 3.14 in the strong coupling limit gives the same Fokker-Planck equation if one defines the dimensionless friction constant as

\[
\alpha = \frac{6\eta \gamma_0}{|\mathbf{m}_i|},
\]

(3.17)

With this definition of \(\alpha\), the strong coupling limit is equivalently found in the case of a very viscous solvent \(\eta \to \infty\), or a very small MNPs, \(\mathbf{m}_i \to 0\). For example the value of \(\alpha\) for a system of five MNPs suspended in water as simulated in Section 5.2.3.1 is \(-1.78 \times 10^3\) making the effective gyromagnetic ratio, \(\frac{\gamma_0}{1 + \alpha^2}\), very small and therefore within the strong friction limit.

3.2 Implementation

In the strong friction limit the only equation of motion that needs to be implemented for the magnetic forces on MNPs is Eqn 3.15. In addition to the magnetic forces we need to take into account translational movement of MNPs as well as collisions between them. To model the remaining components we have used splitting integrators to model the Langevin equation (Eqn 3.1). I will be presenting the algorithm implementation used in the following two sections. The first section goes into detail about the splitting integrator, while the second describes the force field used in the model.

The implementation of the equations of motion have been devised to obtain a good compromise between accuracy and speed to ensure a stable and fast algorithm for the simulation of magnetic nanoparticles in solution. The target accuracy of the algorithm ensures that properties like the total energy and the magnetic moment of the MNP are conserved in the absence of dissipation \([120]\). An increase in the accuracy required will increase the complexity of the integration which will then take longer to solve. An accuracy level must be chosen so that there is a minimal impact on the final result while still providing a fast algorithm. Due to the size of the MNPs we are simulating, our accuracy has been taken to second order, where higher order terms are very small and
can safely be neglected. Information on the implementation of the program, Mango, can be found in Chapter 4.

### 3.2.1 Splitting scheme

Splitting integrators [121] are used to ensure both reversibility (e.g., symmetric with respect to time inversion) and accuracy in the absence of dissipation. Splitting integrators can also be symplectic, in the sense that they preserve the phase space volume. The conservation of the phase space volume is important in order to assure that the simulated system does not morph into a different system, such as a change in the magnitude of the magnetic saturation with each time step. In the case of deterministic (i.e., in absence of dissipation) equations of motion several splitting schemes are also known to be symplectic, i.e. to preserve the phase space volume through the integration. As a consequence, other integrals of motion are conserved by construction [122]. Verlet type algorithms are symplectic and the following sub-steps are calculated at each iteration of the integrator:

<table>
<thead>
<tr>
<th>(a) Position Verlet</th>
<th>(b) Generalised position Verlet for MNPs in a non-magnetic fluid in a magnetic field</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Update</strong></td>
<td><strong>Quantity</strong></td>
</tr>
<tr>
<td>Position</td>
<td>$r' \leftarrow \tau/2 , r_i$</td>
</tr>
<tr>
<td>Momentum</td>
<td>$p' \leftarrow \tau/2 , p_i$</td>
</tr>
<tr>
<td>Stochastic</td>
<td>$p'' \leftarrow \tau, \xi_i , p_i'$</td>
</tr>
<tr>
<td>Momentum</td>
<td>$p_{i+1}' \leftarrow \tau/2 , p_i''$</td>
</tr>
<tr>
<td>Position</td>
<td>$r_{i+1}' \leftarrow \tau/2 , r_i'$</td>
</tr>
<tr>
<td>Momentum</td>
<td>$p_{i+1}'' \leftarrow \tau/2 , p_i'''$</td>
</tr>
<tr>
<td>Position</td>
<td>$r_{i+1}' \leftarrow \tau/2 , r_i'$</td>
</tr>
</tbody>
</table>

In Table 3.1, we show our generalisation of the standard position Verlet to include the effects of MNPs in the model and contrast it to the standard position Verlet for non-magnetic nanoparticles. The dependence on a whole ($\tau$) or half ($\tau/2$) time step, along with a possible dependence on a random number generation ($\xi$), has been indicated above the update arrows. For instance, the momentum is updated twice within one iteration, \( p'_i \) is obtained after a half time step integration of the momentum, \( p''_i \) is obtained after a full time step integration of the stochastic step for the position Verlet.
3.2. Implementation

and a half time step for the generalised position Verlet. For the generalised position Verlet $p_i'''$ is obtained after a second half time step integration of the stochastic step. $p_{i+1}$ is obtained after a second half time step integration of the momentum. The position is also updated twice: $r_i'$ is obtained after a half time step integration and the final position update, $r_{i+1}$ is obtained after a second half time step. In all cases the subscript $i + 1$ is a complete iteration. All primed quantities are temporary quantities.

The coupling of the MNPs to their environment introduces a dissipative mechanism in the dynamics which is then no longer reversible. However a symplectic splitting integrator is still advantageous as it improves the accuracy of the statistical sampling [122]. A generalised position Verlet fulfils the accuracy needs of the system conserving quantities required such as the total energy in a conservative system [67, 123].

With the addition of stochastic steps to the system the total energy is no longer conserved but the stochastic step enables the modelling of a system in a thermal bath. However the volume phase space of the integrator is still conserved which is a requirement of statistical sampling. For non-magnetic particles there would only be one calculation of the force per time step. To include the magnetisation of the particles in the algorithm it has been further split.

The position and momentum updates are based on a first order Taylor expansion of the position and the momentum of the MNP. In practice the position update for both update steps and both position Verlets is approximated as

$$r_i' = r_i + \left( t + \frac{\tau}{2} \right) \frac{p_i}{m_{NP,i}} \tau + O(\tau^2)$$  \hspace{1cm} (3.18)

Position updates are dependent on the current momentum, $p_{i\alpha}$, of each nanoparticle. The momentum update for both update steps is approximated as

$$p_i' = p_i + \left( t + \frac{\tau}{2} \right) f_{i\alpha} \left( r_i + \frac{\tau}{2} \right) \tau + O(\tau^2)$$  \hspace{1cm} (3.19)

where $f_{i\alpha}$ is a conservative force, see Section 3.2.2. The error in the position and momentum equations is second order in $\tau$. Higher order splitting schemes exist such as third order devised by Ruth [124] or fourth and greater devised by Yoshida [122] among others [125]. These higher order methods add complexity to the numerical integration and they do not necessarily allow for an increase in the time step needed to achieve the target convergence threshold [126].

The stochastic step (Eqn 3.20) is applied to the momentum calculated in the second step of both Verlet methods. For the generalised Verlet method the stochastic step is
also applied after the magnetisation update.

\[
p''_{i\alpha} = p'_{i\alpha} e^{-\Gamma \tau_{mNP,i}} + \xi_{tr,i\alpha} \sqrt{k_B T_{mNP,i}} \left( 1 - e^{-\frac{2\Gamma \tau_{mNP,i}}{m_i}} \right) \tag{3.20}
\]

where \( k_B \) is the Boltzmann constant, \( T \) is the temperature of the solvent and \( m_{NP,i} \) is the mass of the \( i \)th MNP [127]. We are in the high friction limit as discussed in Section 3.1.2 therefore \( \Gamma = \Gamma_{tr} \) (see Eqn 3.5). The stochastic propagation shown in Eqn 3.20 is exact for simpler translational Brownian motion described by the Ornstein–Uhlenbeck process which keeps the algorithm reversible [128]. With the addition of the stochastic part the algorithm is no longer reversible due to the coupling with, and allowing the inclusion of, the environment in the model. It is not possible to use the Ornstein–Uhlenbeck process directly because of the need to include the environment in our model. In the stochastic step a random number, \( \xi_{tr,i\alpha} \), is sampled from a normal distribution,

\[
P(\xi_{tr,i\alpha}) = \frac{1}{\sqrt{2\pi}} e^{-\frac{\xi_{tr,i\alpha}^2}{2}} \tag{3.21}
\]

The algorithm used to extract \( \xi_{tr,i\alpha} \) is discussed in Section 3.2.3.

The magnetisation is the most computationally expensive step of the integration, and the only addition to the splitting scheme that was made. It is more efficient to have it at the centre of the iteration step to minimise the number of recalculations per complete iteration therefore a full time step is used [126]. The integration is implicit because it conserves the magnitude of each MNP’s magnetic moment [129, 130]. Calculation of the magnetisation includes a stochastic part (included through \( H_{th} \), Eqn 3.16) to damp the dynamics of the system. The damping dynamics are needed to include the solvent surrounding the MNPs in the simulation.

The implicit midpoint method is used due to its stability over other similar methods [131]. Starting the self-consistent iteration of the implicit midpoint method requires a guess value for the magnetisation, \( m'_i \), at \( t + \tau \) which is set equal to the magnetisation at \( t \), \( m_i \). The normalised average value of \( m'_i \) and \( m_i \) is then computed as

\[
m''_i = |m_i| \frac{U}{|U|} \tag{3.22}
\]

where

\[
U = \frac{m'_i + m_i}{2} \tag{3.23}
\]

The magnetisation is then updated using Eqn 3.15 with \( m_i = m''_i \). Only the inter particle component of the magnetic field (from the dipole-dipole interaction) is updated during the self-consistency iteration. The external field, \( H_{ext} \) as part of the deterministic total magnetic field \( H_{tot} \), and the stochastic component \( H_{th} \) do not depend on the
3.2. Implementation

instantaneous magnetisation and do not need to be computed self-consistently.

A refined guess of the magnetisation at time $t + \tau$ is then obtained as

$$m_i'''(t + \tau) = m_i(t) + \frac{d}{dt}(m_i'')\tau \quad (3.24)$$

using Eqn 3.15 and a new normalised average of $m_i'''$ and $m_i$ is then computed. The self-consistent iteration is continued until the norm of the difference between two subsequent guesses,

$$\Delta|m_i| = \left| \frac{(m_i'''(t - \tau) - m_i(t))}{m_{\text{sat},i} V_p} \right| \quad (3.25)$$

becomes smaller than a threshold value. In all the numerical simulations shown in this thesis, convergence is assumed when $\Delta|m_i|$ gets below the machine precision, $\epsilon_{\text{machine}}$ which for a double precision number is $2.22 \times 10^{-16}$.

The convergence threshold is very stringent in order to minimise a systematic error in the propagation due to an imperfect conservation of the magnitude of each MNP’s magnetic moment. In particular, such a systematic error can accumulate over the large number of time steps which are needed to compute the magnetic autocorrelation function of MNP chains (see Section 3.3.3.1). Our simulations are of the order of $10^7$ time steps, so small systematic errors could have a large effect on the resulting MNP trajectories.

For the simulations shown in Section 5.2, an average number of six self-consistent iterations has been required to converge the implicit midpoint method. System scaling can be seen in Chapter 4. The full algorithm progresses as shown below in Fig. 3.2.
3.2. Implementation

Initial MNP configuration

Position
\[ r'_i \leftarrow r_i \]

Momentum
\[ p'_i \leftarrow p_i \]

Stochastic
\[ p''_i \leftarrow \xi_{rr,i} p'_i \]

Magnetisation
\[ m_{i+1} \leftarrow m_i \]

Stochastic
\[ p'''_i \leftarrow \xi_{rr,i} p''_i \]

Momentum
\[ p_{i+1} \leftarrow p''_i \]

Position
\[ r_{i+1} \leftarrow r_i \]

Final Iteration?

Yes

Final MNP Configuration

No

Yes

\[ \Delta \| m_i \| < \epsilon_{\text{machine}} \]

Figure 3.2: A flowchart of the algorithm as implemented
3.2. Implementation

3.2.2 Force field

To model the translational movement of particles, the dipole interactions between the particles need to be taken into consideration. There are many possible potentials that are widely used for different applications. Each vary in complexity and accuracy for specific situations. The potential used within our system will provide the translational potential as defined in Eqn 3.3 where $U_{\text{tr}}(\mathbf{r})$ will be the desired potential. The most commonly used for general applications is the Lennard-Jones potential \[132, 133\]

$$U_{\text{LJ},i}(\mathbf{r}) = 4\varepsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{\hat{r}_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{\hat{r}_{ij}} \right)^{6} \right]$$ (3.26)

$\sigma_{ij}$ is the notional distance between MNPs $i$ and $j$, $\hat{r}_{ij}$ is the magnitude of the distance between MNPs $i$ and $j$, and $\varepsilon_{ij}$ is the depth of the potential well between $i$ and $j$. The value for $\varepsilon_{ij}$ is fitted from experimental results for the system in question \[134\]. In our case the repulsion strength scales with $\sigma_{ij}$ \[135, 136\]

$$\varepsilon_{ij} = 119.8k_B \left( \frac{\sigma_{ij}}{3.405 \times 10^{-2}} \right)^3.$$ (3.27)

The attractive section of the potential provides the simulation of Van der Waals forces. Van der Waals forces between molecules at an infinite distance are infinitely small, but are a noticeable quantity at atomic scales.

Truncated potentials are widely used to model chains of MNPs \[137, 138\]. MNPs in systems such as chains and colloids are said to be soft shell and bear similarities in dynamics to the interactions of atoms due to Van der Waal’s forces \[139\]. One such potential is the WCA potential \[140\]. The repulsive part of the WCA potential is useful for modelling colloidal suspensions \[141\].

$$U_{\text{WCA},i}(\mathbf{r}) = \begin{cases} 
\varepsilon_{ij} + U_{\text{LJ},i}(\mathbf{r}) & \hat{r}_{ij}/\sigma_{ij} \leq 2^{1/6} \\
0 & \hat{r}_{ij}/\sigma_{ij} > 2^{1/6}
\end{cases}$$ (3.28)

We decided to use the WCA potential for our simulations over the Lennard-Jones potential because of its ability to reproduce experimental results of chains and colloids \[137\].

To use any of these potentials in a simulation you need not just the potential energy that these equations provide but also the forces they induce between the particles of the system as provided by Eqn 3.2 \[142\]. The total magnetic field felt by the $i^{th}$ MNP, (Eqn 3.10) also depends on the instantaneous position and magnetic moment of all other particles.

The force on the $i^{th}$ MNP, $\mathbf{f}_i(\mathbf{m}, \mathbf{r})$, consists of two distinct parts, a soft sphere force,
3.2. Implementation

\( f_{WCA,i}(m,r) \) and the dipole-dipole magnetic interaction, \( f_{\text{mag},i}(m,r) \),

\[
 f_i(m,r) = f_{WCA,i}(r) + f_{\text{mag},i}(m,r) \tag{3.29}
\]

The soft sphere interaction is introduced to model the short range repulsion between particles. To achieve this, the WCA potential was used as seen in Eqn 3.28 [140, 141],

\[
 f_{WCA,i}(r) = \nabla_r U_{WCA,i}(r) \tag{3.30}
\]

The dipole-dipole magnetic potential energy is written as a sum of two-body interaction between magnetic moments as seen in Eqn 3.4, and the inter particle magnetic potential is defined as,

\[
 U_{\text{mag,int}}(m,r) = \sum_{j<i} \frac{1}{r_{ij}^3} \left[ 3(m_i \cdot \hat{r}_{ij})(m_j \cdot \hat{r}_{ij}) - (m_i \cdot m_j) \right] , \tag{3.31}
\]

where \( \hat{r}_{ij} = r_{ij}/|r_{ij}| \) is the Euclidean unit vector between MNPs \( i \) and \( j \). The magnetic component of the force of the \( i \)th MNP is defined as

\[
 f_{\text{mag},i}(m,r) = -\nabla_r U_{\text{mag,int}}(m,r) = -\sum_{j \neq i} \frac{3}{r_{ij}^5} \left[ 5(m_i \cdot \hat{r}_{ij})(m_j \cdot \hat{r}_{ij})\hat{r}_{ij} - m_i(m_j \cdot \hat{r}_{ij}) \right. \\
- (m_i \cdot \hat{r}_{ij})m_j - (m_j \cdot \hat{r}_{ij})m_i \tag{3.32}
\]

3.2.3 Random Numbers

To produce the random numbers needed to create the ‘white noise’ needed for Eqns 3.6 and 3.13 a pseudo random number generator (PRNG) is needed. A PRNG needs a few characteristics to give reliable and reproducible numerical results. In particular, it must be:

- Reproducible
  
  The PRNG must be able to produce the same stream of numbers when requested, known as ‘seeding’ the PRNG. Seeding the PRNG makes simulations reproducible. In physical experiments it is not possible to reproduce the exact experiment again because there will always be uncontrolled errors. With simulation these errors can be minimised.

- Uniformly distributed
  
  The sampling technique must produce numbers that are evenly distributed across the given range so as to not bias some range of numbers. All PRNG generate numbers between 0 and 1, all of which should be equally likely. As a general
rule if the numbers repeat within a single experiment they are probably not random enough. PRNG’s have a predefined period in which the pattern of random numbers will not be repeated [143]. The default in many implementations is the Mersenne Twister which has a very large period of $2^{19937} - 1$ [144]. Having such a long period allows for vast numbers of statistical repetitions each needing a lot of pseudo random numbers without generating the same sequence.

- **High Generation Speed**

Generating pseudo random numbers can be a very computationally expensive process [145]. Minimising the generation time can greatly affect the overall run time of the simulation. Generation of normally distributed random numbers by methods such as the Ziggurat method or the Box-Muller method add to the generation time on top of the underlying generator.

To allow for a greater production rate of statistically uncorrelated trajectories the simulation can be carried out in parallel. Problems arise from the generation of random numbers in parallel. When these numbers are generated in parallel there is a chance that they will generate repeated numbers. To avoid correlation a ‘jump’ function can be employed, e.g., as implemented for the Mersenne twister by H. Haramoto et al. [144]. As the generator is only pseudo random the random numbers, although uniformly distributed, are predictable. We can therefore move or ‘jump’ down the generation order so as to avoid the same string of random numbers for each simultaneous calculation.

The size of the jump must be large enough to avoid superpositions as much as possible during the simulation and therefore it must be larger than the amount of pseudo random numbers generated per individual trajectory. The Mersenne twister was chosen due to the large volume of research that has been carried out into the reliability and stability of the generator [143]. The Ziggurat method was chosen because of the lower computation time required to generate the normally distributed random numbers [146].

### 3.2.4 Summary

In summary to simulate the trajectories of MNPs you need the following equations:

- $r_{\alpha} \left( t + \frac{\tau}{2} \right) = r_{\alpha}(t) + p_{\alpha}(t) \frac{\tau}{2} + \mathcal{O}(\tau^2)$ (Eqn 3.18)
- $p_{\alpha} \left( t + \frac{\tau}{2} \right) = p_{\alpha}(t) + f_{\alpha} \left( r \left( t + \frac{\tau}{2} \right) \right) \frac{\tau}{2} + \mathcal{O}(\tau^2)$ (Eqn 3.19)
- $p''_{\alpha} = p'_{\alpha} e^{-\frac{r_{\alpha}}{m_{\text{NP},\alpha}}} + \xi_{\alpha} \sqrt{k_B T m_{\text{NP},\alpha}} \left( 1 - e^{-\frac{2r_{\alpha}}{m_{\alpha}}} \right)$ (Eqn 3.20)
- $\frac{dm_{\alpha}}{dt} = \frac{\gamma_0}{1+\alpha^2} m_{\alpha} \times \left[ (H_{\text{tot},i} + H_{\text{th},i}) + \frac{\alpha}{m_{\alpha}} m_{\alpha} \times (H_{\text{tot},i} + H_{\text{th},i}) \right]$ (Eqn 3.15)
3.3 Linear Response

Since the equation for the rotational Brownian motion of the MNPs reduce to the stochastic Landau-Lifshitz-Gilbert (sLLG) in the high friction limit, only one set of equations needs to be implemented to describe the complete dynamics of the system as seen in Section 3.1.2. In the general case Eqn 3.14 would also need to be implemented to model the magnetisation changes due to particle rotation.

3.3 Linear Response

To model the linear response of MNPs, a simulation of the MNPs has to be carried out with no external magnetic field applied as was discussed in Section 2.2.1. The simulation should be conducted using the equations in Section 3.2.4.

The linear response of a chain of MNPs in the magnetic field generated by the chain can be decomposed into the rigid body response (from the rigid rotational motion of the chain) and an interparticle response. Interparticle response and motion in this context is the particle motion within the chain. In this section, we show how to calculate the magnetic susceptibility (see Eqn 1.6) from a MNP simulation trajectory. We then show how to decompose the magnetic susceptibility if the timescales of rigid rotation and interparticle motion are sufficiently separated. The decomposition is not an exact method therefore the larger the separation in relaxation timescales the more efficiently the components can be separated. Timescale separations of at least two orders of magnitude are well decomposed.

3.3.1 Debye Relaxation

The magnetic susceptibility, $\chi(\omega)$ of a single spherical or ellipsoidal MNP in solution can be modelled by the Debye model, [147] which states that

$$\chi(\omega) = \frac{\chi_0}{1 + i\omega\tau_D},$$

(3.33)

where $\chi_0$ is the static (zero frequency) magnetic susceptibility of the MNP [118, 148] and $\tau_D$ is its Debye relaxation time. For a sphere of diameter $d$, the relaxation time is given by Eqns 2.9 and 2.10. The Debye susceptibility in the time domain is given by

$$\chi(t - t') = \begin{cases} \chi_0 e^{-\frac{t - t'}{\tau_D}} & \text{if } t > t' \\ 0 & \text{otherwise} \end{cases}$$

(3.34)

The Debye model applies when the magnetic correlations decay exponentially. The Debye relaxation time is only applicable when the particles are axially symmetric (e.g.
spheres and ellipsoids, although ellipsoidal relaxation needs adjustment of the relaxation time, Section 3.3.1.1) and in a dilute solution of MNPs in a non-magnetic liquid. For non-axially symmetric MNPs, contributions to the dynamics due to multiple easy axes will lead to deviations from the Debye model.

The non-magnetic liquid must also be isotropic across timescales much smaller than $\tau_D$ otherwise the dynamics will include variations due to the varying conditions within the liquid [149]. The MNPs must be of similar sizes to obey the Debye theory otherwise the low frequency regime does not follow the same dynamics the theory describes [150]. At low frequencies the inertia of the particles can no longer be neglected and therefore isn’t represented by the Debye model. If particles have a large size distribution (the diameters differ by more than 1-2 orders of magnitude) averaging the relaxation times of the particles will not accurately reflect the dynamics of the system [150].

3.3.1.1 Non-spherical particles and a comparison to chains of spherical particles

MNPs in colloidal suspension tend to aggregate because of the magnetic interaction (along with other factors such as Van der Waals force) [67, 151]. These aggregates contain a mixture of linear chains, rings and more complicated structures that are seen both in numerical and physical experiments [70].

![Figure 3.3: A comparison of a chain of MNPs to an ellipsoid MNP](image)

As a first approximation, a finite rigid chain consisting of identical MNPs of a given diameter can be modelled as a bar. A bar can also be approximated by an ellipsoid with two equal axes (a spheroid). The combination of the two approximations leads to the image shown in Fig. 3.3. The Cartesian equation of an ellipsoid is

$$\left(\frac{x}{a}\right)^2 + \left(\frac{y}{b}\right)^2 + \left(\frac{z}{c}\right)^2 = 1$$

(3.35)

where $a$, $b$ and $c$ are the length of the principal semi-axes. If $a = b = c$ the spheroid reduces to a sphere, whereas if $b = c$ and in the limit of $a \rightarrow \infty$ the spheroids is equivalent to an infinite bar. In both cases we have prolate spheroids since $a > b = c$ see Fig. 3.4. If we define the aspect ratio as $\mathcal{A} = b/a$, for an prolate spheroids we
3.3. Linear Response

always have that $A \leq 1$.

Figure 3.4: A prolate spheroid where semi-axis $b$ (blue) is equal to $c$ (green) is the short axis plane and $a$ (red) is the long axis.

From the work of Perrin [13] where a misprint was corrected by Wyman [152] and Koenig [153], we know that the rotational relaxation time, $\tau_r(A)$ of a prolate spheroid of a given aspect ratio, $A$, is given by

$$\frac{1}{\tau_r(A)} = \frac{1}{3} \left( \frac{1}{\tau_{\parallel}(A)} + \frac{2}{\tau_{\perp}(A)} \right)$$

(3.36)

where $\tau_{\parallel}(A)$ is the relaxation time for rotations about the longitudinal (elongated) axis and $\tau_{\perp}(A)$ is the relaxation time for rotations about a perpendicular transverse axis (short axis) as seen in Fig. 3.4. The longitudinal and transverse relaxations times are given by [13, 152, 153]

$$\tau_{\parallel} = \frac{2}{3} \left[ \frac{1 - A^4}{2 - A^4} \ln \left( \frac{1 + \sqrt{1 - A^2}}{A} \right) \right]$$

(3.37)

$$\tau_{\perp} = \frac{4}{3} \left[ \frac{1 - A^4}{2 - A^4} \ln \left( \frac{1 + \sqrt{1 - A^2}}{A} \right) + 1 \right]$$

(3.38)

where

$$\tau_{B} = \frac{3\eta V_{el}}{k_B T}$$

(3.39)

and $V_{el} = \frac{4}{3}\pi abc$ is the volume of the ellipsoid. Eqn 3.36 gives the Debye relaxation time for a sphere with a volume equal to the ellipsoid. It can be shown that Eqn 3.36
reduces to Eqn 2.10 in the case of a sphere.

Figure 3.5: A graph showing the decreasing relaxation time for increasing aspect ratio, $\mathcal{R}$ as seen in Eqns 3.36 to 3.38. $\tau_r$ is the total ellipsoidal rotational relaxation time, $\tau_{\perp}$ is the ellipsoid rotational relaxation time about the perpendicular axis, $\tau_{\parallel}$ is the ellipsoid rotational relaxation time about the longitudinal axis. The relaxation is of a 10 nm radius (short axis) magnetic ellipsoid suspended in water at $T=300K$ as simulated in Fig. 5.3

The relaxation time decreases for $\tau_r$ and $\tau_{\perp}$, as Fig. 3.5 shows however the parallel relaxation time, $\tau_{\parallel}$ shows a higher order decay for increasing aspect ratio. A relaxation around the transverse axis has a much larger friction per unit volume than a relaxation around the longitudinal axis therefore a small increase in the aspect ratio will not decrease the friction per unit volume as much along the transverse axis but it will decrease the friction per unit volume for the longitudinal axis quite drastically. Therefore the relaxation time around $\tau_{\parallel}$ decays much more rapidly than $\tau_{\perp}$ as the aspect ratio becomes larger. When the aspect ratio is close to that of a sphere the logarithmic terms become negligible. At small aspect ratios when the ellipsoid approaches the dimensions of a wire the logarithmic terms become the dominant terms in the equation.
3.3. Linear Response

3.3.2 Calculation of the Specific absorption rate

The fluctuation dissipation theorem states that the linear response of a given system to a small external perturbation can be expressed in terms of the fluctuation properties of the system in thermal equilibrium [14]. Small fluctuations occur naturally in a system in thermal equilibrium. These thermal fluctuations are introduced in the simulations by means of the stochastic process $\xi(t)$, see Eqns 3.16 and 3.20.

In a system at equilibrium like a MNP solution, the fluctuations depend on the viscosity of the solvent fluid, $\eta$, the magnetisation of the MNPs, as well as the temperature of the environment.

According to the fluctuation-dissipation theorem the amount of power absorbed, $P$ from a sinusoidal external RF source, $H_{ext}(t) = H_0 \cos(\omega t)$, where $H_0$ is the the field strength, is related to the imaginary part of the magnetic susceptibility as already shown in Eqn 1.7. Finally, the SAR of the system is defined as the power absorbed per unit mass of the MNP [93]. Commonly the SAR is taken per unit mass of the magnetic element which for LSMO is manganese [26]. For instance, in the case of a spherical MNP of LSMO35 that has:

- a density, $\rho$, of 6.99 g cm$^{-3}$,
- a radius of 10 nm,
- a magnetic density, $m_\rho$, of 85 emu g$^{-1}$,

in a system where,

- $T = 300$ K
- $\eta = 1.002 \times 10^{-2}$ g cm$^{-1}$ s$^{-1}$

and the alternating magnetic field has,

- a frequency of 175 kHz ($1.09 \times 10^6$ rad/s),
- and a field amplitude of 137.6 Oe,

and $\chi_0$ is calculated from [150]

$$\chi_0 = \frac{(\rho m_\rho)^2}{V_\rho k_B T} = 4081 , \quad (3.40)$$
3.3. Linear Response

therefore using Eqns 2.10 and 3.33

\[ \text{Im}\{\chi(\omega)\} = 3.27, \quad (3.41) \]

and using Eqn 1.7 the specific absorption rate is

\[ \text{SAR} = \frac{P}{\rho} = \frac{0.5 \cdot 3.27 \cdot 1.09 \times 10^6 \text{rad/s} \cdot (137.6 \text{ Oe})^2}{6.99 \text{ g cm}^{-3}} \cdot 10^{-7} \text{ erg/J} \quad (3.42) \]

= 487 W g\(^{-1}\)

3.3.3 Implementation

The trajectories saved by the simulation do not include all time steps. Due to the accuracy required in the integrator, a small time step of less than 100 ps is used. Larger time steps result in changes in the dynamics that are too large for the integrator to keep the difference in the magnetisation between steps less than \(\varepsilon_{\text{machine}}\) (Eqn 3.25). To compute the magnetic susceptibility (Eqn 3.51), a coarser sampling of every 2000 time steps suffices. The simulation takes time to equilibrate to the required temperature, \(T\). The processing of the trajectory must be carried out after the equilibration and the equilibration is hence removed from the trajectory before any processing takes place. To ensure the system is equilibrated the trajectory is processed after 10\% of the trajectory or \(2 \times 10^4\) samples.

3.3.3.1 Magnetic autocorrelation function

The magnetic susceptibility in Eqn 3.33 is computed from the magnetic autocorrelation function (MACF). The MACF is defined as [154]

\[ \phi_{\alpha\beta}(t) = \lim_{A \to \infty} \frac{1}{A} \int_{-\frac{A}{2}}^{\frac{A}{2}} \Delta M_{\alpha}(t') \Delta M_{\beta}(t + t') \, dt' \quad (3.43) \]

where \(A\) is the propagation time and

\[ \Delta M_{\alpha}(t) = \sum_{i=1}^{N} (m_{i\alpha}(t) - \bar{m}_{i\alpha}) \quad (3.44) \]

is the difference between total magnetisation, i.e., the sum of the single MNP magnetisation, where \(N\) is the number of sampled time steps and the average magnetisation is

\[ \bar{m}_{i\alpha} = \lim_{A \to \infty} \int_{-\frac{A}{2}}^{\frac{A}{2}} m_{i\alpha}(t) \, dt \quad (3.45) \]
3.3. Linear Response

In practice, the average magnetisation becomes vanishingly small for long enough trajectories due to the random rotations of the chain. To speed up the calculations, instead of computing the time integral in Eqn 3.43 directly, we use the properties of the Fourier transform (FT). In particular the FT of the autocorrelation function is proportional to the (normalised) magnetic density of states (MDOS) tensor, \( \rho_{\text{mag,}\alpha\beta}(\omega) \),

\[
\tilde{\phi}_{\alpha\beta}(\omega) \propto \rho_{\text{mag,}\alpha\beta}(\omega) = \frac{\left| \Delta \tilde{M}_\alpha(\omega) \Delta \tilde{M}_\beta^*(\omega) \right|^2}{\sum_{\alpha=1}^{3} \int_{-\infty}^{\infty} \left| \Delta \tilde{M}_\alpha(\omega) \right|^2 d\omega},
\]

(3.46)

where the FT of the total magnetisation is defined as [155].

\[
\Delta \tilde{M}_\alpha(\omega) = \int_{-\infty}^{\infty} \Delta M_\alpha(t) e^{-i\omega t} dt.
\]

(3.47)

Zero padding of the data is also used to improve the signal [156]. In practice, all FT are taken as discrete FT [126] over a finite, yet large, number of samples. In our case, the FT is taken over \( 1.8 \times 10^5 \) time step samples. The MDOS is defined as the trace of the MDOS tensor,

\[
\rho_{\text{mag}}(\omega) = \sum_{\alpha=1}^{3} \rho_{\text{mag,}\alpha\alpha}(\omega),
\]

(3.48)

and is invariant with respect to rotations of the reference frame. In particular, we have diagonalised \( \rho_{\text{mag,}\alpha\alpha}(\omega) \) and verified that two out of the three eigenvalues are vanishingly small due to the magnetic anisotropy of the MNP chains being aligned with shape anisotropy axis. For a single spherical MNP all eigenvalues are equal as there is no overall anisotropy. The non-vanishing eigenvalue corresponds to the MDOS projected onto the chain long axis. Due to the anisotropy of the MDOS tensor, it makes sense to consider only the trace of the magnetic autocorrelation function,

\[
\tilde{\phi}(\omega) = \sum_{\alpha=1}^{3} \tilde{\phi}_{\alpha\alpha}(\omega) \propto \rho_{\text{mag}}(\omega),
\]

(3.49)

where the constant of proportionality is determined by the normalisation,

\[
\lim_{t \to 0} \phi(t) = \lim_{A \to \infty} \frac{1}{A} \int_{-\frac{A}{2}}^{\frac{A}{2}} \left| \sum_{i=1}^{N} (m_{ia}(t) - \overline{m}_{ia}) \right|^2 dt.
\]

(3.50)

Finally, the magnetic susceptibility of the system is obtained from the MDOS as

\[
\chi(\omega) = \frac{\omega \tilde{\phi}(\omega)}{2k_B TNV_p}.
\]

(3.51)
3.3. Linear Response

3.3.3.2 Block averages

A trajectory of any system is inherently correlated from one time step to the next. A set of effectively uncorrelated samples is obtained by skipping a number of time steps in the trajectory. In order to assess the number of magnetic correlation times,

\[ N_{\text{mag,corr}} = \frac{t_{\text{sim}}}{\tau_D} , \]  

(3.52)

where \( t_{\text{sim}} \) is the simulation time, we use the standard block averaging method [157].

The aim of a blocking analysis is to correctly estimate the statistical errors of a particular observable. In a molecular dynamics simulation, the standard deviation of any dependent property of the system is underestimated because the number of independent measurements is much smaller than the total number of measurements. The standard deviation of a measurement only converges on the true value as the number of measurements approaches infinity [158]. Blocking of data is a decorrelation technique to acquire a good estimate of the standard deviation [157].

According to the block average method, the trajectory is split in \( N_b \) blocks and the average magnetisation is computed for each block

\[ M_{s\alpha} = \frac{1}{N_b} \sum_i m_{s\alpha} \]  

(3.53)

\[ \overline{M}_{k\alpha} = \frac{1}{N_b} \sum_{s \in S_k} M_{s\alpha} , \]  

(3.54)

where \( k = 1, \ldots, N_b \) is the block index, \( S_k \) are the indices of the time steps in the \( k \)th block and \( s \) is the indices of the unskipped time steps. In this thesis, we will only consider disjoint blocks so that the intersection of any two sets of indices is empty. The average magnetisation is then rewritten as the average of the blocks

\[ \overline{M}_{\alpha} = \frac{1}{N_b} \sum_{k=1}^{N_b} \overline{M}_{k\alpha} \]  

(3.55)

and the variance as

\[ \sigma^2_\alpha(\overline{M}_{\alpha}) = \frac{1}{N_b(N_b-1)} \sum_{k=1}^{N_b} \left( \overline{M}^2_{k\alpha} - \overline{M}^2_{\alpha} \right) \]  

(3.56)

The block average estimate of the variance, Eqn 3.56, presents a plateau when the length of the block (e.g. the cardinality of \( S_k \)) exceeds the correlation length, but it is still much smaller than the total number of steps (see Fig. 3.6). As a rule thumb, we
required a trajectory to be at least ten times longer than the magnetic correlation time i.e., $N_b \geq 10 N_{\text{mag,corr}}$, to have a sufficiently converged block average estimate.

Below a block size containing ten correlation times, uncaptured oscillations can create artefacts in the MDOS of the trajectory. The artefacts stem from the time between each sample being larger than the oscillation frequency of the magnetic correlation. The longer the trajectory the more such artefacts are damped out according to $e^{t_p \tau}$ where $t_p$ is the period of time the trajectory covers [159]. The block average method can be applied to every observable. For instance, the variance of the magnetic susceptibility has been estimated as [160]

$$
\sigma_p^2(\chi(\omega)) = \frac{1}{N_b(N_b-1)} \sum_{k=1}^{N_b} (\chi_k^2(\omega) - \chi^2(\omega)) .
$$

Figure 3.6: Dependence of Standard Deviation on Block size. Panel a) shows the average magnetisation of 96 independent simulated trajectories of a single MNP with a radius of 10 nm as simulated in Fig. 5.3 at different numbers of blocks. The error bars are the standard deviation between the trajectories. b) shows the change in the standard deviation with increasing number of blocks.

Fig. 3.6 examines the effect of increasing the number of blocks in the block average
3.3. Linear Response

method on average magnetic moment of a MNP. The plateau in panel b) of Fig. 3.6 the standard deviation is about 50% larger than the standard deviation reported by using a single block per trajectory. To achieve an accurate estimation of the errors the number of blocks would need to be increased by an order of magnitude. However the size of the errors are 4 orders of magnitude smaller than the average value therefore, although underestimated, the errors only change the prediction minutely.

3.3.3.3 Kabsch Algorithm

Given two sets of particle configurations, one at time \( t \), \( \{r_{i\alpha}(t)\} \) and one at time 0, \( \{r_{i\alpha}(0)\} \), where \( i = 1, \ldots, N \) is the particle index and \( \alpha = x, y, z \) is the coordinate index, the root mean squared deviation (RMSD) is defined as [161]

\[
RMSD = \sqrt{\frac{1}{N} \sum_{i\alpha} (r_{i\alpha}(t) - r'_{i\alpha}(0))^2}, \tag{3.58}
\]

Note that the particles are assumed to be distinguishable. A common problem in molecular dynamics is to separate the rigid motion of a set of particles from their interparticle motion. For the sake of simplicity, here we assumed that the two configurations have been centred, i.e., that their centre of mass has been already subtracted from the particle coordinates, so that the rigid motion is obtained through an appropriate rotation.

The Kabsch algorithm gives the optimal rotation which minimises the RMSD of the centred two particle configurations [161, 162]. In the case of a MNP chain, we first centre all the configurations of a trajectory by removing the centre of mass momentum, then we align the initial configuration, \( \{r_{i\alpha}(0)\} \) along the x-axis, finally we use the Kabsch algorithm to align each configuration to the initial one.

In particular, Kabsch’s algorithm makes use of a singular value decomposition (SVD) [126] of the matrix

\[
S_{\alpha\beta} = \sum_{i=1}^{N} r_{i\alpha}(t)r_{i\beta}(0), \tag{3.59}
\]

where the \( \beta \) index is the aligned coordinate index, which is decomposed as

\[
S_{\alpha\beta}(t) = \sum_{\gamma} V_{\alpha\gamma}(t)\Lambda_{\gamma}(t)W_{\gamma\beta}(t), \tag{3.60}
\]

where \( \gamma \) is a tertiary axis, the axis of the singular values, \( V \) is the first rotation matrix, \( A \) is the diagonal scaling matrix and \( W \) is the final rotation matrix to acquire the original matrix \( S_{\alpha\beta} \). Using the SVD, the optimal rotation can be written as [162]

\[
R(t) = W^T(t)U(t)V^T(t), \tag{3.61}
\]
where
\[ U = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \text{sgn}(\det \Lambda) \end{pmatrix}. \] (3.62)

Using the rotational matrices, \( \{R_{\alpha\beta}(t)\} \), it is possible to separate rotational dynamics from the interparticle dynamics by writing the instantaneous centred configurations as
\[ r_{i\alpha}(t) = R_{\alpha\beta}(t)[r_{i\beta}(0) + \Delta r_{i\beta}(t)], \] (3.63)
where \( \Delta r_{i\beta}(t) \) represents the interparticle motion in the rotating reference frame.

The same set of rotations can be applied to the separate rotational dynamics from the interparticle dynamics of the total magnetisation as follows
\[ M_{\alpha}(t) = \sum_{\beta} R_{\alpha\beta}(t) [M_{\beta}(0) + \Delta M_{\beta}(t)], \] (3.64)
where \( \Delta M_{\beta}(t) \) represents the interparticle motion in the rotating reference frame. By means of Eqn 3.64, the MACF can be rewritten as
\[ \sum_{\alpha} \langle M_{\alpha}(t)M_{\alpha}(0) \rangle = \sum_{\alpha\beta} \langle R_{\alpha\beta}(t) [M_{\beta}(0) + \Delta M_{\beta}(t)] M_{\alpha}(0) \rangle \\
= \sum_{\alpha\beta} \langle R_{\alpha\beta}(t)M_{\beta}(0)M_{\alpha}(0) \rangle \\
+ \sum_{\alpha\beta} \langle R_{\alpha\beta}(t)\Delta M_{\beta}(t)M_{\alpha}(0) \rangle, \] (3.65)
where \( \langle R_{\alpha\beta}(t)\Delta M_{\beta}(t)M_{\alpha}(0) \rangle \) is for the interparticle diffusion of a stiff object such as the movement of particles within a chain and the \( \langle R_{\alpha\beta}(t)\Delta M_{\beta}(t)M_{\alpha}(0) \rangle \) accounts for the flexible diffusion of a chain as can be seen in Fig. 3.7.
The inter particle diffusion of a chain can be approximated to

\[
\sum_{\alpha\beta} \langle R_{\alpha\beta}(t) M_{\beta}(t) M_{\alpha}(0) \rangle \simeq \sum_{\alpha\beta} R_{\alpha\beta}(0) \langle \Delta M_{\beta}(t) M_{\alpha}(0) \rangle \\
= \sum_{\alpha} \langle \Delta M_{\alpha}(t) M_{\alpha}(0) \rangle \\
= \sum_{\alpha} \langle (\Delta M_{\alpha}(t) + M_{\alpha}(0)) (\Delta M_{\alpha}(0) + M_{\alpha}(0)) \rangle - \langle M_{\alpha}(0) \rangle^2.
\]

(3.66)

We assume that \( R_{\alpha\beta}(0) = \delta_{\alpha\beta} \) where \( \delta_{\alpha\beta} \) is the Kronecker delta. Therefore we are also assuming that the initial magnetisation is aligned along the same axis for all statistical repetitions of the simulation. This assumption is only valid without loss of generality in the case of no external field as is the case with our simulations. Finally it is assumed that the changes to the residual magnetisation, \( \Delta M_{\beta}(t) \), happen at a time-scale around 100\times faster than \( R_{\alpha\beta}(t) \) as can be seen in Chapter 5 in Figs. 5.5 and 5.6. The physical origin of this is the increased relaxation time of an ellipsoidal MNP as aspect ratio increases (Section 3.3.1.1). Therefore we assume that the optimal rotation matrix is unchanged between consecutive residual magnetisation changes i.e. \( R_{\alpha\beta}(t) \simeq R_{\alpha\beta}(0) \). When we sum over \( \alpha \), the rotational matrix \( R_{\beta}(0) \) is a delta function at all points.

The autocorrelation function of the rotational and residual component sum to give the autocorrelation function of the total magnetisation giving a method to examine different modes of the magnetisation trajectory.

Figure 3.7: The initial overall magnetisation of a MNP chain, \( M_{\alpha}(0) \) in a) can be aligned with an arbitrary axis in b) using the rotation matrix \( R_{\alpha\beta}(0) \) to attain \( M_{\beta}(0) \). After a time, \( t \), c) shows the overall magnetisation of the MNP chain is \( M_{\alpha}(t) \). Using the rotation matrix \( R_{\alpha\beta}(t) \) the chain is aligned in d) to the same axis as b). In d) the overall magnetisation is \( M_{\beta}(0) + \Delta M_{\beta}(t) \).
3.3.4 Summary

In summary to post process a MNP trajectory using linear response theory and to separate the inter particle and rigid motion of a chain the following equations are needed:

Calculation of the magnetic susceptibility, Eqn 3.51

\[ \chi(\omega) = \frac{\omega \tilde{\phi}(\omega)}{2k_B TNV_p} \]

The rotational matrix separation, Eqns 3.65 and 3.66

\[ \sum \langle M_\alpha(t) M_\alpha(0) \rangle = \sum \langle R_{\alpha\beta}(t) [M_\beta(0) + \Delta M_\beta(t)] M_\alpha(0) \rangle \]

\[ \sum \langle R_{\alpha\beta}(t) \Delta M_\beta(t) M_\alpha(0) \rangle = \sum \langle (\Delta M_\alpha(t) + M_\alpha(t)) (\Delta M_\alpha(0) + M_\alpha(0)) \rangle - \langle M_\alpha(0)^2 \rangle \]

The separation of the rigid rotational relaxation and the interparticle relaxation is not an exact process therefore the sum of the rotational and interparticle MDOS (and therefore magnetic susceptibility) might be larger than the total MDOS.
Chapter 4

Program Design

The program, Mango, is a molecular dynamics simulator for magnetic nanoparticles, designed to be as versatile as possible. The name is derived from MAGnetic NanOpar-
ticle. The word magnet is derived from the Greek region Magnesia, where we also get the name for Manganese and a reason for our spelling mistake of MAGNO, to provide us with the name Mango [163].

Included with Mango is the ability to post process the data produced in the simulations including some complete post processing tools as described in Section 3.3.3. Mango is written in Python because we have found Python to be a good compromise between expressiveness and optimisation through the available linear algebra libraries, SciPy [164, 165] and NumPy [165, 166].

The use of NumPy and SciPy allows for the use of low level functions that are written in C. For instance the `einsum` function of NumPy allows for the vectorisation of tensor products, while keeping the readability of Python. Our Python program uses fewer lines of code than lower level languages such as FORTRAN or C, leading to a more transparent implementation. Our program can be found at https://mangocode.gitlab.io.

4.1 Capabilities

Mango is able to simulate magnetic nanoparticles while allowing the user to determine different properties of materials. The capabilities include:
4.1. Capabilities

- Modifiable magnetic and interparticle potentials
  By default, as described in Chapter 3, Mango is set up with the WCA potential and the magnetic dipole-dipole potential. To completely replace the potentials a module would need to expose two functions for the interparticle potential and 3 functions for the magnetic potential. Currently it is possible to write magnetic and translational potentials in any language importable into Python such as C/C++ or FORTRAN.

- Data Management
  For post processing outside the tools built into Mango it is possible to directly access the simulation data for external processing.

- Energies
  Calculation of kinetic and potential energies of each particle along with the forces on the particle. Kinetic temperature of the system is calculated from the linear momentum (Section 4.2.5).

- Linear and angular momenta
  The linear and angular momenta along with the moment of inertia are calculated from the MNP trajectories.

- Autocorrelation
  Both the autocorrelation functions and density of states is calculable for the velocity, angular momentum, inertia and magnetisation.

Each of these points are examined in detail in the following sections. The main design aim of Mango is to have a low barrier to entry to remove as many program barriers as possible. Enabling the user to concentrate on the science rather than in depth programming, while still providing programming options, has created an easy to use but powerful simulation program.

4.1.1 Ease of Use

The application interface of Mango allows for use of both the command line and an interactive interface like the Jupyter Project [167]. In addition a plain text input file can be specified to simplify the job submission to a computer cluster. Examples of three equivalent setup’s of a five particle simulation are shown in Fig. 4.1. For further examples in this chapter I will only show the python input. The input file uses the same keywords as the python file and is therefore transferable. The command line has very similar but slightly different input criteria due to the limitations of the input method. Command line input is used for submitting an input file but is not the recommended to
4.1. Capabilities

be used directly (although completely possible). All the customisable parameters have a set of defaults for simulating LSMO MNPs that can be adjusted to the simulation requirements as needed. To change the type of MNP used in the simulation the user needs to specify the MNP density and the MNP magnetic density as seen in the example calculation in Fig. 4.17. A full list of input file parameters with brief explanations and default values can be seen in Appendix A. Full explanations to the parameters can be found throughout this chapter.

a)

```
mango --suscep -n 100000 -st 1 -np 5 -P './Position_file'
```

b)

```
import mango
mango.run({'SusceptibilityCalc': True, 'Iterations': 100000, 'Repetitions': 1, 'NumberParticles': 5, 'PositionFile': './Position_file'})
```

c)

```
SusceptibilityCalc    True
Iterations            100000
Repetitions           1
NumberParticles       5
PositionFile          './Position_file'
```

d)

```
mango -I InputFile
```

Figure 4.1: A simple 5 MNP simulation set up using a) The command line, b) A python file, c) An Input file, and d) shows how to submit an input file from the command line.

The position file specified in Fig. 4.1 can be a file with a list of xyz coordinates for the centres of each MNP or more precisely as a frame of a (extended) xyz file as seen in Fig. 4.2. The extended frame of the xyz file includes the positions of each MNP, with the addition of the momentum, magnetic field strength and forces associated with the MNP.
5.07e-01 -5.59e+00 -9.78e+00 1.54e-01 2.16e-02 -1.08e-01
7.00e+01 -1.65e+01 1.76e+03 -7.23e-07 1.00e-06 4.68e-06

Figure 4.2: A frame of the extended xyz file with each line wrapped.

The user has the ability to customise many parameters of the simulation from the environment, through modification of viscosity and temperature, to the compressibility of the MNP by changing the depth of the potential well. For the benefit of the end user it is possible to export all positional data to an (extended) xyz file in the post processing of the simulation. Along with xyz files, Mango will output momenta and energy data of the MNPs as shown in Section 4.1.4.

### 4.1.2 Modifiable magnetic and interparticle potentials

To replace the default WCA interparticle potential it is possible to specify another included potential (currently limited to the Lennard-Jones potential, Eqn 3.26) or write a simple script with two functions that calculate the forces and energies on the MNPs. Calculation of energies associated with the MNPs is not carried out during the simulation, but is a post processing tool as explained in Section 4.1.4. The decision was made to postpone energy calculations to decrease the time taken to complete a run.
from numpy import einsum, add, subtract

__all__ = ['vv_trans', 'ff_trans']

def vv_trans(self):
    
    """Lennard Jones Potential.""
    self.lj6[:] = (self.sigma * self.rij)**6
    self.epot_tr[:] = 4 * self.epsilon * self.lj6 * (self.lj6 - 1)

def ff_trans(self):
    
    """Calculate Translational Force.""
    self.force_trans[:] = 0
    self.lj6[:] = (self.sigma * self.rij) ** 6
    einsum("i, ij, i-> ij",
    self.epsilon24 * (2. * self.lj6 - 1.) * self.lj6,
    self.rijz, self.rij * self.rij, out=self.ftrans)

    subtract.at(self.force_trans, self.ia, self.ftrans)
    add.at(self.force_trans, self.ja, self.ftrans)

Figure 4.3: A complete python file of the Lennard-Jones potential

Using the Lennard-Jones potential python script seen in Fig. 4.3 (an implementation of Eqns 3.26 and 3.30) it is reasonably simple to create a new interparticle potential by simply creating two functions; ‘vv_trans’ which modifies the ‘self.epot_tr’ variable and ‘ff_trans’ which modifies the ‘self.force_trans’ variable containing the resultant translational force for all particles.

To replace the default magnetic dipole-dipole potential, three functions, ‘vv_mag’, ‘ff_mag’ and ‘hh_mag’ need to be replaced. These functions return the magnetic potential energy, magnetic force and magnetic field strength respectively as seen below in Fig. 4.4.
4.1. Capabilities

```python
__all__ = ['vv_mag', 'ff_mag', 'hh_mag']

def vv_mag(self):
    """Magnetic potential Energy."""
    [...]
    return mag_pot

def ff_mag(self):
    """Calculate Magnetic Force."""
    [...]
    return mag_force

def hh_mag(self):
    """Calculate Magnetic field strength."""
    [...]
    return hfield
```

Figure 4.4: An example of functions needed to replace the magnetic potential

If the magnetic and interparticle potentials are to be replaced, the python files in Figs. 4.3 and 4.4 would need to be combined into a single script. To use the potential in a simulation it needs to be specified in the input as seen in panel a) of Fig. 4.5. The included potentials are selected with its file name within the './mango/potentials/' folder eg. ‘LennardJones6_12’ for the built in Lennard-Jones potential as shown in panel b) of Fig. 4.5.

a)

```python
mango.run({[...], 'Potential': './LJpotential.py'})
```

b)

```python
mango.run({[...], 'Potential': 'LennardJones6_12'})
```

Figure 4.5: How to specify a) A new potential b) A built in potential

4.1.3 Data Management

The output file generated by a Mango simulation can be specified as one of these three formats: a basic plain text output, the internal Python format ‘pickle’ and the HDF Group’s HDF5 n-dimensional datasets binary file format [168]. The HDF5 format is the most portable of the three and can be read by many programming languages through a number of interfaces [168]. By default the datasets within the HDF5 file are compressed using the blosc compression algorithm which is known for its speed of I/O while still
compressing the file [169]. HDF5 dataset can be read incrementally removing the need to decompress the whole file on access.

As Mango is written in Python it is easily integrated into other projects. The program is designed so as to be easily usable in part or in full by importing specific modules such as the I/O module. Processing data outside of Mango’s post processing tools from a simulation is achieved using ‘read_data’ from the ‘mango.io’ module.

```python
from mango.io import read_data

reader = read_data('Example.1.hdf5')
print(reader.read(keylist=True))
mnp_pos = reader.read('position')
[...]
```

Figure 4.6: Manually reading in data for processing

In Fig. 4.6 we show how it is possible to access the position data of the MNPs from an example simulation file. Accessing a list of possible keys gives the user precise control over the data enabling further processing of specific subsets of the saved data such as the MNP positions. In this instance a key is the storage device used to store the name of a variable associated with a given set of values, known as a key/value pair.

### 4.1.4 Energies and Momenta

Accessing data on the energies and momenta involved in the system is achieved from an input as shown in Fig. 4.7.

```python
mango.run({'LogDirectory': './', 'Run': 1,
[...], 'CreateFile': ['energy', 'momenta']})
```

Figure 4.7: Creating energy and momenta files

The energy and momenta files produced by post processing in Mango is not per particle but for the whole system. The energy file provides columned data on kinetic energy, translational potential energy, magnetic potential energy and Total energy (the sum of the three constituent energies) as shown in the segment of the energy file in Fig. 4.8. The momenta file provides columned data on the angular momentum, magnetisation momentum and the total momentum of the system.
4.1. Capabilities

<table>
<thead>
<tr>
<th>#itern.</th>
<th>time</th>
<th>kinetic_e</th>
<th>pot_tr</th>
<th>pot_mag</th>
<th>total_e</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.00e+00</td>
<td>0.00e+00</td>
<td>0.00e+00</td>
<td>-1.11e-05</td>
<td>-1.11e-05</td>
</tr>
<tr>
<td>1</td>
<td>8.00e+02</td>
<td>3.51e-06</td>
<td>8.33e-08</td>
<td>-1.09e-05</td>
<td>-7.32e-06</td>
</tr>
<tr>
<td>2</td>
<td>1.60e+03</td>
<td>3.01e-06</td>
<td>8.37e-08</td>
<td>-1.06e-05</td>
<td>-7.55e-06</td>
</tr>
</tbody>
</table>

Figure 4.8: A segment of an energy file

It is possible to directly access the per particle energy and momenta data by reading from the data file using ‘read_data’, as shown previously, with the short script shown in Fig. 4.9.

```python
import mango.io as mio
import mango.pp.main as mpp
import mango.pp.energy as me
reader = mio.read_data('Example.1.hdf5')
flg = mpp.get_ppflags(reader)
var = mpp.get_ppvars(flg, reader)
e_mdata = me.get_eandm(reader, var)
print(e_mdata.keys())
```

Figure 4.9: How to retrieve energy and momenta data

The retrieved data is a python dictionary containing all of the constituent parts of the energy and momenta of the system.

4.1.5 Autocorrelation

The autocorrelation function and density of states of various properties of the MNPs can be calculated directly using the post processing tools in Mango. In our work we have examined the magnetic susceptibility which is derived from the magnetic density of states (MDOS) as seen in Eqn 3.51. It is also possible to calculate the autocorrelation function and density of states of velocity, angular momentum and inertia of the MNPs by specifying the desired option(s) to ‘SusceptibilityCalc’ shown in Fig. 4.10.

```python
mango.run({'LogDirectory': './', 'Run': 1,
            [...], 'SusceptibilityCalc': ['mag'])
```

Figure 4.10: Manually reading in data for processing

The possible options for each of the autocorrelations are ‘mag’, ‘vel’, ‘angular’, ‘inertia’ and ‘rotation’. The ‘rotation’ option is a special option to calculate the magnetic
rotational dynamics of a MNP chain as described in Section 3.3.3.3, and must be used in conjunction with the ‘Align’ option as seen in Section 4.3.2.

When a simulation is processed to create autocorrelation data, two files creating the autocorrelation function and the density of states of the property are created. Both files contain 7 columns, the first being time for the autocorrelation function, and angular frequency for the density of states. The remaining columns are 3 columns for the spatial dimensions of the autocorrelation data and 3 columns for the standard deviation of the autocorrelation data.

4.2 Implementation Details

4.2.1 Periodic Boundary Conditions

It is not feasible to model a large material at the nanoparticle level or smaller due to the amount of time it will take to compute the interactions between each particle and all other particles in any simulated system. To reduce the computational load, while enabling the simulation of large systems of particles, periodic boundary conditions can be used. Periodic boundary conditions set boundary conditions around a minimal unit of the system, called the unit cell. The boundary condition allows for the simulation of an infinitely large system. The unit cell is a minimal unit of the simulated material that when replicated would form the whole material. When a particle passes through the boundary at one edge of the cell it re-appears at the opposite boundary. To avoid interactions with a periodic ‘image’ (a particle interacting with itself) the boundary needs to be large enough so any interactions are negligible. For isolated systems the boundary needs to be large enough so that all image interactions are negligible.

The periodic positions are calculated using

\[ \mathbf{r}_{\text{pbc}} = \mathbf{r} - \left( \mathbf{BOX} \cdot \left\lfloor 0.5 + \frac{\mathbf{r}}{\mathbf{BOX}} \right\rfloor \right) \]  

where \( \lfloor x \rfloor \) is the nearest integer value less than or equal to the value specified, known as the floor function. The size of the periodic unit cell is specified by the \( \mathbf{BOX} \) vector and is currently limited to orthogonal unit cells in Mango. Periodic boundary coordinates in Mango originate at the centre of the unit cell.

The periodic boundary conditions are applied to the interparticle distances every time the positions of the MNPs are updated but only applied to the positions after each timestep as the positions are not needed in the calculation of the interparticle forces. The wrapping can be seen in Fig. 4.11 in the ‘boundaries:wrapping’ function which is
called 3 times per iteration plus 3 calls to set up the system.

4.2.2 External Magnetic field

The external applied magnetic field properties can be adjusted by setting values for the input file keys ‘ExternalFieldFreq’ and ‘ExternalFieldStrength’. You can run a zero field calculation by setting ‘SusceptibilityCalc’, in which case the external field variables are ignored essentially setting both to zero. The simulations shown in this thesis are all zero field simulations and therefore do not include an external applied field.

4.2.3 Néel Relaxations

Basic Néel relaxations using the linear response theory (Section 2.2.2.2) can be enabled in Mango simulations setting ‘NeelRelaxations’ in the input but are not enabled by default. Néel relaxations are implemented using the Poisson probability distribution which gives the probability of an event happening (in the case of a MNP undergoing a Néel relaxation) in a given time period [170].

\[
P(N_n \text{ events in } \tau) = \frac{\lambda^{N_n} e^{-\lambda}}{N_n!}
\]  

(4.2)

where the average number of relaxations per time step, \( \lambda = \tau / \tau_N \) and \( N_n \) is the number of Néel relaxations. For our uses we calculate the probability of a single relaxation happening within one time step. We assume that only one relaxation can occur within a time step therefore \( N_n = 1 \). At each time step the probability of a relaxation is then compared to a random number between 0 and 1, if the random number is greater than the probability the relaxation has occurred.

When a relaxation takes place the magnetisation of the MNP is inverted as described by the linear response theory in Section 2.2.2.2 [86]. The Néel relaxation time is controlled by the three keys ‘NeelAnisotropicFactor’ \( (K_u) \), ‘NeelTau0’ \( (\tau_0) \) and ‘NeelTemp0’ \( (T_0) \) as seen in Eqns 2.2 and 2.3.

Although implemented in Mango we have not simulated any systems in this thesis with Néel relaxations because the added complexity increases the difficulty to pinpoint the root cause of simulation artefacts.
4.2. Implementation Details

4.2.4 Zero temperature relaxations

Mango is capable of relaxing an initial configuration of particles to reduce the energy of the initial configuration and the forces between the MNPs by using sequential least squares method implemented in NumPy to adjust the positions and magnetisations of the MNPs [171]. The relaxation is achieved by minimising the translational potential and magnetic potential energies along with the translational force and magnetic force between MNPs. The relaxation is undertaken when the ‘Optimisation’ key is specified in the input. In addition to the relaxation it is possible to give the MNPs the thermal momentum associated with the temperature of the simulation using the ‘ThermalOptim’ key in the input.

\[ p_{\text{therm}} = \sqrt{m_{\text{NP}} k_B T} \]  

(4.3)

The thermal momentum is the width of the peak of the Maxwell-Boltzmann distribution giving us the typical momentum of a MNP as seen in Eqn 4.3, we then apply the product of the momentum and a uniformly generated random vector to the MNPs [172].

4.2.5 Kinetic Temperature

In the post processing of a simulation, the kinetic temperature can be calculated from the linear momentum of the system using the ‘KineticTemp’ key in the input. The kinetic temperature is calculated by fitting the average velocity of the MNPs to the Maxwell-Boltzmann speed distribution [172]

\[ D_{\text{mb}}(v) = \frac{m_{\text{NP}} / 2}{\Gamma(\frac{3}{2}) v^2_{\text{fit}}} \exp \left( -\frac{m_{\text{NP}} v^2_{\text{fit}}}{2} \right) \]  

(4.4)

where \( \Gamma(x) \) is the gamma function and

\[ v_{\text{fit}} = \sqrt{k_B T} \simeq v_{\text{avg}} \left( \frac{m_{\text{NP}}}{2} \right)^{1/2} \frac{\Gamma(\frac{3}{2})}{\Gamma(2)} \]  

(4.5)

The approximate value for \( \sqrt{k_B T} \) is fitted using the Levenberg-Marquardt least squares algorithm implemented in NumPy to approximate the kinetic temperature [173].

4.2.6 Program Structure

Mango is designed in a modular way to allow for the addition of new features without completely rewriting the program. The procedure that Mango undertakes during a
simulation can be seen in Fig. 4.11 where $10^6$ iterations are carried out on a chain of 5 MNPs. There is a very distinct critical path where most of the simulation time is spent that leads to the calculation of the magnetisation of the MNPs which takes up 65% of simulation time. The single most critical component to the speed of Mango is NumPy’s einsum function as stated in the introduction to this chapter. Nearly all functions are dependent on the matrix multiplication that einsum is capable of (it is called ~120 times per iteration) and is therefore the main engine of the program.

Mango is parallelised from ‘magnetic_motion:run’, this function and all of its children can be run in parallel working on different statistical repetitions from the initial setup with a different random number stream. A single iteration starts with the ‘position:propagate’ function and it is the root of the majority of the internal mechanics of Mango.

The ‘magnetic_motion:disksaveloop’-‘magnetic_motion:memorysaveloop’-‘magnetic_motion:skiploop’ chain is the functions that control the I/O of Mango as described in Fig. 4.12 before it written to disk using the ‘magnetic_motion:file’ function and its children. The ‘magnetic_motion:finaliteration’ function manages runs with uncommon numbers of iterations such as those indivisible by the number of iterations held in memory before writing to disk.
4.2 Implementation Details

Figure 4.11: A callgraph of a $10^8$ iterations Mango simulation from Fig. 4.1 with the 5 MNP positions generated in a chain using ‘mango_strings’ as seen in Fig. 4.15. The colour of each region represents the percentage time spent in the function. The dark blue boxes represent less than 15% of the time, green boxes represent 15 to 65%, and red boxes are greater than 95%. Each function box contains the function name, the percentage time spent in the function and its children, and the number of times the function is called. The function name in each function box contains the module name, the line number within the module and the function name itself. In brackets is the percentage run time inherited from the parent and the number of time the parent calls the child function.
4.2.7 Optimisations

Mango has been optimised to make efficient use of the available computational resources. The computational efficiency has been improved by pre-calculation of many properties that can be reused throughout a simulation.

Efficiencies have been introduced by using mathematical devices such as the Levi-Civita tensor converting a cross product into a matrix product. Dot products can then in turn be efficiently calculated using the use of NumPy interfaces to optimised LAPACK routines. The Python wrapper, pyFFTW, has been used to wrap the well known FFTW library enabling fast parallel calculation of Fourier transforms [174, 175].

The statistical sampling of independent trajectories can be made embarrassingly parallel [176]. Each run is completely independent because every run is initialised with a different random number seeding. Mango can run in parallel using both the internal...
4.2. Implementation Details

Python multiprocessing library for local (single node or desktop) simulations or embarrassingly parallel MPI implementations supported by the mpi4py library. The use of MPI gives Mango the capability to run on anything from a laptop to multi-node clusters.

Saving of the simulation data happens in two stages when running the main calculation as shown in Fig. 4.12. Reducing the amount of I/O to disk by using more of the system RAM reduces the number of times the output file needs to be opened reducing the program overhead for file writing. As not every iteration is needed for all types of molecular dynamics post processing some can be discarded reducing the final file size of the simulation storage file.

To reduce the danger of loosing data and to control the amount of RAM needed for a simulation, the trajectory data is saved at user configurable intervals to an output file using the ‘SaveChunk’ parameter.

4.2.8 System Requirements

The main bottleneck for Mango simulations is the speed of the processor on the computer. On an Intel Xeon e5-2650 v4 @2.2 GHz the simulation seen in Fig. 5.5 takes 118hrs or just under 5 days to complete.

Mango’s memory requirements are very small compared to the current size of memory in even the smallest computer available today. For each extra iteration that is saved to memory Mango saves 12 double precision numbers per particle which require 8 bytes of storage each. A long simulation, such as the 5 MNP simulation mentioned above, runs for $4 \times 10^8$ iterations but only saves every 2000 iterations as stated in Section 5.2. We therefore save $2 \times 10^5$ iterations during the simulation which is around 20 MB per MNP simulated if the whole simulation was left in memory for the whole run. There is of course other information that needs to be stored behind the scenes to run the program but it is far below the gigabytes of memory available to most computers. With all of the extras, a 5 MNP simulation requires around 200 MB to store the whole run in memory per processor (and therefore as a Mango run is embarrassingly parallel per statistical repetition).

Saving the required data to file requires slightly more in order to preserve the structure of the data as well as information on the initial conditions of the run. For the same 5 MNP simulation a single file will require around 500 MB of disk space. The amount of disk space space as with memory per processor is repeated per statistical repetition.
4.2.9 Scaling

The number of self-consistent iterations of Mango’s implicit midpoint integrator (see Section 3.2) per step does not depend on the number of MNPs, as shown in Fig. 4.13. In comparison the number of magnetisation calculations used by Omelyan et al. is explicitly $2N - 1$ calculations per MNP (LAMMPS line in Fig. 4.13) [177]. As the number of magnetic calculations needed for Mango is constant in the limit of very large systems Mango will take less physical time to complete a simulation.

![Figure 4.13: The number of magnetisation calculations needed for chains of MNPs of increasing lengths for Mango and LAMMPS. The simulations to produce the Mango data points were carried out on 10 nm radius LSMO35 MNPs suspended in the centre of a 10 µm periodic boundary in an implicit solvent with the viscosity of water. The LAMMPS scaling is the theoretical scaling from [177]](image)

For systems with more than five particles Mango needs to perform less calculations of the magnetisation than the integrator described by Omelyan et al. and recently included in LAMMPS which require recalculation the magnetisation for each magnetic spin in the system [177, 178]. In Mango’s implicit integrator (described in Section 3.2) the number of self-consistent calculations shown in Fig. 4.13 is an average. Therefore the number of self-consistent calculations per step is not fixed and the Mango line in Fig. 4.13 is the average number of self-consistent calculations, the standard deviation
of which is of the order of $10^{-2}$. Both methods are able to compute the dynamics of MNPs but for large systems LAMMPS will have to do many more recalculations of the magnetisation therefore in the limit of large numbers of MNP Mango will compute the dynamics in a shorter amount of physical time.

The physical time scaling of Mango is shown below in Fig. 4.14, as you can see Mango does calculate less simulated time as the number of MNP increases although it is a much slower decrease than that of LAMMPS.

Figure 4.14: The length of simulated time calculated by LAMMPS and Mango per second of physical time for different lengths of MNP chains. The simulations to produce this figure were carried out on 10 nm radius LSMO35 MNPs suspended in the centre of a 10 µm periodic boundary in an implicit solvent with the viscosity of water.

LAMMPS is quicker at simulating the small systems here than Mango under the same conditions but as the number of MNPs in the system increases there is a large decrease in the simulated time completed per second. If the trend continues as expected Mango would be faster than LAMMPS when large number of MNPs are being simulated.

In the current version of the code only the statistical sampling of the independent trajectories has been parallelised as each statistical repetition is embarrassingly parallel. Further speed up can be obtained by the parallelisation of the force field evaluation
and integration algorithm. However this is a speed up based on the availability of more processors so it would not be a speed improvement of the code itself.

4.3 Example Calculation

For an example calculation, I will show how to setup a simulation of a 2 MNP chain of LSMO35 as we simulated in Fig. 5.4. The MNPs will be simulated with no external magnetic field, in water and will be 20 nm in diameter. The simulation in the example will be run with the ‘mpi_run’ command (Fig. 4.17) and therefore use embarrassingly parallel MPI for the simulation. To run without MPI ‘mpi_run’ can be replaced with the ‘run’ command. Currently there is no MPI developed for post processing and therefore only the ‘run’ command is used. However within post processing, libraries such as FFTW mentioned in Section 4.2.7 can make use of multiple cores within the same processor using the OpenMP shared memory library. In the post processing of the simulation I will show how the data for the graph in Fig. 5.4 is created along with some other processing methods.

4.3.1 MNP simulation

To start a simulation first a position file is needed. As stated earlier in Section 4.1.1 an xyz file is used. In this simulation we are starting the simulation from stationary particles to avoid any external input in order to examine the random motion of the MNPs. We can generate an xyz file for the chain using the helper function built into Mango as seen in Fig. 4.15.

```
mango_strings -h
mango_strings 1.0%1.0 2 0 0 0 0
```

Figure 4.15: Generating an xyz file for a chain of 2 MNPs

The generation of the xyz file in Fig. 4.15 has a few options about how to set up the chain. Firstly ‘1.0%1.0’ is the radius of the MNPs and the buffer zone around the particles as a percentage of the radius. The separation of the particles is to reduce the chance of the MNPs violently repelling each other at the beginning of the simulation. The next number is the number of MNPs, in our case ‘2’. The following four zeros are the azimuthal angle and the polar angle for the orientation of the MNPs in space and the the azimuthal angle and the polar angle for the orientation of the magnetic moment of the MNPs. By default the positions are aligned along the z-axis of the simulation.
region and the magnetic moments are aligned along the z-axis of each MNP.

```
# Generated with mango strings generator
MNP  0.00e+00  0.00e+00  -1.01e+00  0.00e+00  0.00e+00
     0.00e+00  0.00e+00  0.00e+00  1.00e+00
MNP  0.00e+00  0.00e+00   1.01e+00  0.00e+00  0.00e+00
     0.00e+00  0.00e+00  0.00e+00  1.00e+00
```

Figure 4.16: Position input file for a 2 MNP simulation

The resulting file in Fig. 4.16 is included in the input for the simulation as seen in Fig. 4.17 under the file name ‘2partchain.xyz’.

```
import mango
mango.mpi_run({'PositionFile': './2partchain.xyz',
               'NumberParticles': 2, 'ParticleDensity': 6.99,
               'ParticleRadius': 1.0, 'MagneticDensity': 85,
               'SusceptibilityCalc': True,
               'Temperature': 300, 'MediumViscosity': 0.01002,
               'PeriodicBoundaries': True, 'Boxsize': 1000,
               'Iterations': 4e8, 'Repetitions': 96, 'Timestep': 20,
               'SkipSave': 2000, 'SaveChunk': 100,
               'SaveFiletype': 'hdf5', 'Walltime': 172000})
```

Figure 4.17: Two MNP simulation script

The input file above has some self explanatory particle parameters such as ‘PositionFile’, ‘NumberParticles’ and ‘ParticleRadius’, some expected environment variables such as ‘Temperature’ and ‘MediumViscosity’, and run parameters such as ‘Iterations’, ‘Timestep’ and ‘SaveFiletype’.

Other particle parameters are ‘ParticleDensity’ which is the density of the MNP and ‘MagneticDensity’ which is the magnetisation per unit mass of the MNP. Further parameters about the system include ‘PeriodicBoundaries’ which enables cubic periodic boundary conditions, ‘Boxsize’ which defines the size of the periodic box the simulation is carried out in and ‘SusceptibilityCalc’ is a setting to include no external applied magnetic field to the system. Excluding the external applied magnetic field enables the examination of the movement of the MNPs in an isolated environment. In our case the box size is large to avoid any interaction with the periodic image of the MNPs.

The remaining parameters control the production of statistical repetitions and the
behaviour of Mango. ‘SkipSave’ controls how many steps as skipped before saving a step to memory and ‘SaveChunk’ controls how often the computer memory is written to file as seen in Fig. 4.12. ‘Walltime’ controls how long Mango runs before exiting which is useful if you have a maximum program run time on a cluster. Running the resultant python script will run the simulation and the simulation can be restarted after hitting a maximum walltime using an automatically generated restart file that is created at the end of Mango’s run. The restart submission is shown below.

```python
mango.mpi_run({'RestartFile': './Run1Restart'})
```

Figure 4.18: How to restart a stopped simulation

### 4.3.2 Post processing

Once the simulation has been completed it can be post processed directly using Mango’s built in tools. To process any data using Mango there are four commands which inform where the data is stored, what form it is in and how to manipulate it.

```python
mango.run({'LogDirectory': './', 'Run': 1, 'SusceptibilityCalc': True, 'Blocking': 96})
```

Figure 4.19: Minimal post processing input

As Fig. 4.19 shows, these four input parameters are all compulsory parameters. They are the folder location on the system, the run number to differentiate between simulations in the same folder, ‘SusceptibilityCalc’ informs whether the simulation was run with an applied external magnetic field. ‘Blocking’ governs how statistics are managed by Mango as discussed in Section 3.3.3.2. The maximum number of blocks should not exceed the number of statistical repetitions produced by the simulation in order to avoid a case where sections of different trajectories are spliced together. If the default ‘hdf5’ file type is not used ‘SaveFiletype’ would also need to be specified.

To extract the data for the graphs shown in Fig. 5.4 the MDOS needs to be calculated as stated in Section 4.1.5. The MDOS is calculated for this simulation with the modification of the ‘SusceptibilityCalc’ key as shown in Fig. 4.20.
4.3. Example Calculation

To calculate the MDOS of the magnetic rotational dynamics as described in Section 3.3.3.3 a separate post processing run is required. With the ‘Align’ option set the Kabsch algorithm is carried out producing data files for the MACF and MDOS of the magnetic rotational dynamics and interparticle dynamics.

Other post processing options include calculation of the average nearest neighbour interparticle distances which is useful for checking to see how straight chains of MNPs are on average. Checking the distances is achieved with the addition of the keyword ‘LengthCheck’ in Fig. 4.21. We have used the option to produce Table 5.4.

As stated earlier in this chapter it is possible to calculate energy and momenta data as described in Section 4.1.4 and an extended xyz file can be created by setting the same ‘CreateFile’ parameter seen in Fig. 4.7 to ‘xyz’.

```python
mango.run({[...], 'SusceptibilityCalc': ['mag']})
mango.run({[...], 'SusceptibilityCalc': ['mag', 'rotation'], 'Align': True})
```

Figure 4.20: Minimal post processing input

```python
mango.run({[...], 'LengthCheck': True})
```

Figure 4.21: Calculation of interparticle distances
Chapter 5

Results

In this chapter we have focussed on the linear response of nanoparticles suspended in water. We have used the stochastic Landau-Lifshitz-Gilbert (Eqn 3.15) in the strong friction limit as described in Section 3.1. As the viscosity of water is $1.002 \times 10^{-2} \text{ g cm}^{-1} \text{s}$, the friction constant, $\alpha = -1.78 \times 10^3$ (see Eqn 3.17) making the effective gyromagnetic ratio is very small putting us in the strong friction limit described in Section 3.1. The force field used in all simulations was the WCA potential for the translational force as stated in Section 3.2.2.

Through benchmarking of Mango we found that the largest time step we could achieve with LSMO was 20 ps. Larger time steps lead to a more unstable integrator where the self consistent magnetisation loop could not calculate the interparticle magnetic field. Smaller time steps had no effect on the results produced apart from being able to resolve dynamics that occur within smaller time scales of which there were none that were not captured at a time step of 20 ps for our uses.

All simulations in this Thesis were carried out with a large periodic boundary size of 10µm to ensure there is no interaction with periodic images (Section 4.2.1) this is around 18 times larger in each axis than if the 55 MNP in Fig. 5.2 were set up end on end.

5.1 Agglomerates

From a single spherical MNP in a periodic box (Section 4.2.1) that can be analytically described as shown in Section 3.3.1, the next logical step is an agglomerate of monodis-
Agglomerates of MNPs. An agglomerate of MNPs is a natural starting point for further analysis of MNP systems.

Agglomerates of MNPs take a long time to completely relax as seen in Fig. 5.1. The kinetic temperature of an agglomerate relaxes quickly to the equilibrium temperature set by the simulation but the potential energy takes around 2 µs to reach equilibrium. With the length of simulation we can simulate for a 55 MNP agglomerate we cannot reach equilibrium within reasonable timescales and conduct a simulation of long enough duration after equilibration to gather any statistically significant data.

The translational potential energy will equilibrate at the same rate as the kinetic temperature. However the magnetic potential energy has many local minima and therefore takes a lot longer to equilibrate.

The dynamics of a MNP system can lead to eventual agglomeration due to the lower potential energy of agglomerated MNPs. The simplest form of agglomeration is chains. As can be seen in Fig. 5.2 small chains do form in the time that can be simulated as shown by the red highlighted particles.

![Figure 5.1: A simulation of a 55 LSMO35 MNP agglomerate at T=200K, with a radius of 10nm. The upper panel shows the relaxation of the potential energy (Eqn 3.3), which is normalised to the initial value of the potential energy, and the lower panel shows the relaxation of the kinetic temperature (Section 4.2.5)](image)
5.2 Chains

In this section we have used the stochastic Landau-Lifshitz-Gilbert (Eqn 3.15) in the strong friction limit as described in Section 3.1 to simulate the linear response of chains of nanoparticles suspended in water. We have then calculated the MDOS from a Fourier transform of the total magnetisation according to Eqn 3.46. The magnetic susceptibility has been calculated according to Eqn 3.51. Where present, the rotational and aligned MDOS and magnetic susceptibility are calculated from the rotational and aligned magnetisation generated by using Kabsch’s algorithm (Section 3.3.3.3). From the magnetic susceptibility it is possible to calculate the specific absorption rate at a known frequency using Eqn 3.42.

5.2.1 Simulation Details

In all of the following simulations all averages and errors have been obtained from 96 trajectories generated in parallel by using different random number streams. The MNPs were arranged to be centred in the simulation box and aligned along the z-axis with the initial magnetisation also aligned along the z-axis. As was discussed in Section 3.3.3.2, the errors are expected to be slightly underestimated in the low frequency limit due to the number of events captured within the simulation (Fig. 3.6). A compromise was made between having a very accurate statistical sampling and modelling the chain response at much lower frequencies.

We modelled two different dopant quantities of LSMO, firstly a strontium dopant of 0.35 (LSMO35) and secondly a dopant of 0.4 (LSMO40). These two dopant’s of LSMO were experimentally described by McBride et al. (2017) with SAR values for bulk quan-
For LSMO35, we first simulated MNPs with a radius of 10 nm at 5 different chain lengths, 1, 2, 5, 10 and 20 MNPs, to see whether the chain acted as an ellipsoid with the same dimensions as the MNP chain (Fig. 3.3) and, if it did not, at what point did the chain stop acting with the same dynamics as a single MNP ellipsoid. We approximated the ellipsoidal dimensions of the chain with $b = c = \text{MNP radius}$ and $a = 2b(N-1)$ where $N$ is the number of nanoparticles.

Before the simulations were run we needed to calculate how long the simulation needed to be to acquire a good statistical representation of the system. As discussed in Section 3.3.3.2 we decided we needed around $10N_{\text{mag,corr}}$. To estimate the relaxation time in Eqn 3.52 before the simulation we used a simple multiple of the Brown relaxation time, $\tau_B$ of a single MNP as our total relaxation time. Our simulations do not include Néel relaxations therefore the Debye relaxation time $\tau_D = \tau_B$. We chose to run all simulations for the maximum possible time we could simulate in order to acquire as much data on the MNP dynamics, our chain length was therefore limited by the $10N_{\text{mag,corr}}$ of our longest chain.

The longest simulation we could run within the our allotted limit of 7 days is around $\sim 4\times10^8$ steps for a chain of 20 MNPs. We estimated that 10% of the trajectory would be needed to equilibrate the system leaving $3.6 \times 10^8$ steps for practical analysis. Our time step limit is 20 ps as discussed at the beginning of this chapter. We therefore could simulate a maximum of $7.2 \times 10^{-3}$ s in $3.6 \times 10^8$ steps leading to our estimated values for the magnetic correlation times, shown below in Table 5.1.

Secondly we simulated LSMO35 MNPs with a 20 nm radius to see how radius, and by extension volume, affected the dynamics of the MNP chain. For this larger radius we did not simulate the shorter 1 and 2 MNP chains due to the dynamics of the system produced by Mango matching quite precisely theoretical models of an ellipsoid (Section 3.3.1.1) for 10 nm radius MNPs (see Fig. 5.4). For the single MNP case our result agreed with the Debye model in Section 3.3.1 as seen in Fig. 5.3.

Our estimations of $N_{\text{mag,corr}}$ shown in Table 5.1 predicted a value greater than 10. When we conducted the 20 MNP chain simulation with a radius of 10 nm, the fitted value for $\tau_B$ was less than 10 (7.24 see Table 5.2). We therefore concluded that we would not be able to produce statistically significant results for the larger radius 20 MNP chain.

The 10 nm MNPs of LSMO35 have a mass of $2.928 \times 10^{-17}$ g and the 20 nm MNPs have a mass of $2.342 \times 10^{-16}$ g. Both particle sizes had a magnetic saturation, $m_{\text{sat}}$ of $5.94 \times 10^2$ emu cm$^{-3}$ therefore the magnetic moment of the 10 nm MNPs is $2.489 \times 10^{-9}$ emu.
and the magnetic moment of the 20 nm MNPs is $1.99 \times 10^{-8}$ emu.

Table 5.1: Estimated number of magnetic correlation times

<table>
<thead>
<tr>
<th>MNP</th>
<th>10 nm</th>
<th>20 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\tau_B$(fit)[s]</td>
<td>$N_{\text{mag,corr}}$</td>
</tr>
<tr>
<td>1 (exact)</td>
<td>$7.2 \times 10^{-3}$</td>
<td>$3.04 \times 10^{-6}$</td>
</tr>
<tr>
<td>2</td>
<td>$7.2 \times 10^{-3}$</td>
<td>$6.08 \times 10^{-6}$</td>
</tr>
<tr>
<td>5</td>
<td>$7.2 \times 10^{-3}$</td>
<td>$1.52 \times 10^{-5}$</td>
</tr>
<tr>
<td>10</td>
<td>$7.2 \times 10^{-3}$</td>
<td>$3.04 \times 10^{-5}$</td>
</tr>
<tr>
<td>20</td>
<td>$7.2 \times 10^{-3}$</td>
<td>$6.08 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

For LSMO40 we simulated 5 and 10 MNP chains with a radius of 10 nm to compare how different dopant quantities affected the dynamics of the MNP chain. The number of magnetic correlations for LSMO40 MNPs with a radius of 10 nm will be the same as for LSMO35. As Eqn 2.10 shows $\tau_B$ is only affected by the properties of the implicit fluid surrounding the MNPs and the volume of the MNP therefore Table 5.1 gives the estimated number of magnetic correlations for all MNPs of the given sizes. With the higher strontium dopant quantity LSMO40 is very slightly lighter than LSMO35 for the same MNP size with a mass of $2.900 \times 10^{-17}$ g. The magnetic saturation is smaller for LSMO40 at $1.61 \times 10^2$ emu cm$^{-3}$ therefore the magnetic moment of the 10 nm MNPs is $6.73 \times 10^{-10}$ emu.

As was discussed in Section 3.3.3.2 every step in a molecular dynamics simulation is not needed in order to produce a good statistical representation of the simulation therefore we recorded every 2000 time steps for our simulations of $4 \times 10^8$ steps. Skipping this amount of data reduces the highest frequency we can observe statistically to 25 MHz which equates to $2.38 \times 10^2 \omega \tau_B$ for 10 nm radius MNPs and $1.91 \times 10^3 \omega \tau_B$ for 20 nm radius MNPs where $\tau_B$ is the relaxation time of a single MNP. The length of our simulations allows us to resolve frequencies as small as 125 Hz which is $1.19 \times 10^{-3} \omega \tau_B$ for 10 nm radius MNPs and $9.54 \times 10^{-3} \omega \tau_B$ for 20 nm radius MNPs.

After simulating these long simulations it was noticed that the magnetic susceptibility curves of 5 LSMO35 MNP chains or longer do not follow a Debye like curve at high frequencies (see Fig. 5.5). To examine the dynamics further at higher frequencies, simulations were carried out with a higher fidelity (i.e. a smaller skip). We reduced the skip from 2000 to 200 increasing our highest resolvable frequency by a factor of 10. We also reduced the simulation to $3.6 \times 10^7$ steps to produce the same number of data points for analysis. The side effect of the shorter simulations is that we cannot resolve the lower frequencies available in the lower fidelity, longer simulations, this is a compromise due to data storage limitations. All of these higher fidelity simulations
were already equilibrated at the starting MNP positions for the simulation were taken from the final step of the lower fidelity counterpart. Other than the skip and step changes the high and low fidelity simulations have identical properties.

For simulations of 5 or more MNP frames of the simulations can be seen in Appendix C to show visible dynamics of the systems.

5.2.2 Analytical result comparisons and fitting

The analysis of the MDOS and magnetic susceptibility was carried out using the Kabsch algorithm discussed in Section 3.3.3.3. The rotational MDOS is calculated from the decomposition of the total MDOS using Eqns 3.65 and 3.66. The magnetic susceptibility is then calculated from each of the total, aligned and rotational MDOS using Eqn 3.51.

With the exception of the single MNP case, in each figure a fit of $\tau_B$ in the Debye model (Eqn 3.33) has been carried out for the rotational magnetic susceptibility in the low frequency region. In the single MNP case both the rotational and total magnetic susceptibility are equal by definition as there is no interparticle motion therefore the fit is calculated from the total magnetic susceptibility only. For both 1 and 2 MNP simulations the fit is calculated using only Eqn 3.33. In the higher frequency region for chains of five MNPs and longer a second fit is carried out from the total magnetic susceptibility. The final fit equation for chains longer than five MNPs is

$$\chi_{\text{fit}}(\omega) = \frac{\chi_{c,0}}{1 + i\omega \tau_B(\text{fit})} + \frac{\chi_0}{1 + i\omega \tau_B},$$

(5.1)

where $\tau_B(\text{fit})$ is the fitted $\tau_B$ from the fit of the rotational magnetic susceptibility. The static magnetic susceptibility of the chain, $\chi_{c,0}$, is calculated from the average magnetic moment of the MNP chain calculated from the simulation.

$$\chi_{c,0} = \frac{\langle \mathbf{m}_i \rangle}{k_BT}$$

(5.2)

The fit equation in Eqn 5.1 is the sum of two Debye models of the magnetic susceptibility (Eqn 3.33) with different relaxation times which correspond to the relaxation time of the chain ($\tau_B(\text{fit})$) and the relaxation of a single MNP ($\tau_B$). The value of $\chi_0$ for the LSMO35 MNP with a radius of 10nm is $1.19 \times 10^1$ and for a radius of 20nm $\chi_0 = 9.52 \times 10^1$, for LSMO40 MNP with a radius of 10nm $\chi_0 = 8.71 \times 10^{-1}$. The relevant frequency range for the fit is denoted by the grey hashed region in all magnetic susceptibility graphs.

In all figures ‘Debye’ denotes the prediction of the Debye model for a single MNP (see Eqn 3.33), ‘Fit’ denotes the fitted line created using Eqn 5.1 (for 1 and 2 MNP, and
LSMO with a strontium fraction of $x = 0.4$ (LSMO40) MNPs Eqn 3.33 is used instead). The magnetic susceptibility and the MDOS from the Debye model is normalised with $\chi_0$ (see Eqn 3.40). All MDOS and magnetic susceptibility graphs have been further normalised to the single MNP Debye model using Eqn 3.51 so that the peak of the single MNP Debye model is one. The ellipsoidal approximation is the analytical relaxation time for an ellipsoid with the dimensions of the chain as seen in Eqn 3.36 and in figure legends is denoted by ‘Equivalent ellipsoid’.

5.2.3 LSMO35

5.2.3.1 10 nm Radius

In Fig. 5.3 we have simulated the linear response of one spherical MNP of LSMO35 in water. This is a low fidelity simulation therefore the raw data was recorded every 2000 time steps. From the magnetisation data we calculated first the MDOS using Eqn 3.46 and then the magnetic susceptibility using Eqn 3.51. The total magnetic susceptibility is compared against the analytical Debye susceptibility, Eqn 3.33.
The excellent agreement between the numerical results and analytic expression over five orders of magnitude provides an early validation of our approach.

There is a numerical artefact at the high frequency of the MDOS and magnetic susceptibility where ‘Total’ deviates from the Debye model and the fit. The deviation is due to the highest frequencies only being partially sampled by the combination of the skip of 2000 and the 20 ps time step. We can confirm this in the higher fidelity simulations where the artefact disappears at the same frequency but reoccurs at the highest frequencies of the simulation (for example Figs. 5.5 and 5.6).

The numerical value for $\tau_B(\text{fit})$ is within error of the analytical value for the Debye model leading to a correct estimate of $\tau_B$ from Table 5.1. All values for $\tau_B(\text{fit})$ calculated from the simulation can be seen in Table 5.2 along with the calculated number of
magnetic correlation times. For the one MNP simulation in Fig. 5.3 we are well above our \(10N_{\text{mag,corr}}\) rule of thumb.

**Table 5.2: The number of correlation times for each low fidelity simulation for 10 nm radius MNPs**

<table>
<thead>
<tr>
<th>N</th>
<th>Time [s]</th>
<th>(\tau_B(\text{fit})) [s]</th>
<th>(N_{\text{mag,corr}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (exact)</td>
<td>7.2 \times 10^{-3}</td>
<td>3.04 \times 10^{-6}</td>
<td>2.37 \times 10^{3}</td>
</tr>
<tr>
<td>1</td>
<td>7.2 \times 10^{-3}</td>
<td>3.02(2) \times 10^{-6}</td>
<td>2.37 \times 10^{3}</td>
</tr>
<tr>
<td>2</td>
<td>7.2 \times 10^{-3}</td>
<td>9.94(4) \times 10^{-6}</td>
<td>7.24 \times 10^{2}</td>
</tr>
<tr>
<td>5</td>
<td>7.2 \times 10^{-3}</td>
<td>9.26(6) \times 10^{-5}</td>
<td>7.78 \times 10^{1}</td>
</tr>
<tr>
<td>10</td>
<td>7.2 \times 10^{-3}</td>
<td>4.152(8) \times 10^{-4}</td>
<td>1.73 \times 10^{1}</td>
</tr>
<tr>
<td>20</td>
<td>7.2 \times 10^{-3}</td>
<td>9.95(3) \times 10^{-4}</td>
<td>7.24</td>
</tr>
</tbody>
</table>

It is also worth noting that the value for \(\chi_{c,0}\) should equal \(\chi_0\) in this single MNP case which it does as both quantities are 1.19 \times 10^3 (the first and second entry in Table 5.3, another validation of the program). All \(\chi_{c,0}\) values for LSMO35 MNP chains with a 10 nm radius are shown in Table 5.3.

In Fig. 5.4 we have simulated the linear response of a chain of two spherical MNPs of LSMO35 in water. This is another low fidelity simulation therefore the raw data was recorded every 2000 time steps. There is a noticeable redshift of the total magnetic susceptibility peak with respect to the Debye model from a frequency of \(1/\tau_B \text{ rad s}^{-1}\) (equivalent to 5.24 \times 10^4 Hz) to 3.058(1) \times 10^{-1}/\tau_B \text{ rad s}^{-1} (1.6010(6) \times 10^4 Hz).

The observed red-shift can be rationalised using the ellipsoidal approximation described in Section 3.3.1.1. The average rotational relaxation time, \(\tau_r\) of an ellipsoid is calculated using Eqn 3.36 and for two MNP chain is equal to 7.10 \times 10^{-6} s as seen in Table 5.3, the fit of \(\tau_B(\text{fit}) = 9.94(4) \times 10^{-6} \text{ s}\). The small discrepancy between the prediction of the ellipsoidal approximation and the simulation can be explained by a shorter chain length than the notional length of the chain (2\(\sigma_{ij}\), the diameter of two MNPs).

The MDOS of the chain after alignment (‘Aligned’ on the legend) is not frequency dependent for a two MNP system as Fig. 5.4 shows. The alignment of the MDOS is calculated using the Kabsch algorithm, see Eqns 3.64 and 3.66, and is not frequency dependent because any interparticle motion between the two MNPs affects the whole chain.
Calculating the turning point of the total magnetic susceptibility is simply $\tau_B^{(\text{fit})}/\tau_B^{(\text{exact})}$ allowing for each access to the highest point of magnetic susceptibility. The theoretical ellipsoid ($\tau_r$) is qualitatively the same as the simulated chain although quantitatively there is a redshift from the ellipsoid to the chain. The calculated values for $\tau_r$ are smaller than the $\tau_B^{(\text{fit})}$ for chains of two or more MNPs suggesting a chain of MNPs does not follow the same dynamics as an ellipsoidal MNP with the same dimensions.
Table 5.3: $\chi_{c,0}$, $\tau_B$(fit) and $\tau_r$, for different chain lengths of 10 nm MNPs.

<table>
<thead>
<tr>
<th>MNP</th>
<th>$\chi_{c,0}$</th>
<th>$\tau_r$[s]</th>
<th>$\tau_B$(fit)[s]</th>
<th>Fit Limits</th>
</tr>
</thead>
<tbody>
<tr>
<td>1(exact)</td>
<td>$1.19 \times 10^1$</td>
<td>$3.04 \times 10^{-6}$</td>
<td>$3.04 \times 10^{-6}$</td>
<td>--</td>
</tr>
<tr>
<td>1</td>
<td>$1.19 \times 10^1$</td>
<td>$3.04 \times 10^{-6}$</td>
<td>$3.02(2) \times 10^{-6}$</td>
<td>[2, 30]</td>
</tr>
<tr>
<td>2</td>
<td>$2.24 \times 10^1$</td>
<td>$7.10 \times 10^{-6}$</td>
<td>$9.94(4) \times 10^{-6}$</td>
<td>[1, 30]</td>
</tr>
<tr>
<td>5</td>
<td>$4.73 \times 10^1$</td>
<td>$2.47 \times 10^{-5}$</td>
<td>$9.26(6) \times 10^{-5}$</td>
<td>[0.2, 10] &amp; [10, 150]</td>
</tr>
<tr>
<td>10</td>
<td>$4.92 \times 10^1$</td>
<td>$5.63 \times 10^{-5}$</td>
<td>$4.152(8) \times 10^{-4}$</td>
<td>[0.05, 3] &amp; [10, 150]</td>
</tr>
<tr>
<td>20</td>
<td>$5.06 \times 10^1$</td>
<td>$1.19 \times 10^{-4}$</td>
<td>$9.95(3) \times 10^{-4}$</td>
<td>[0.05, 1] &amp; [10, 150]</td>
</tr>
</tbody>
</table>

The fit limits are the data ranges used to fit $\tau_B$(fit) in units of $\tau_B$ for a single MNP calculated using Eqn 2.10.

In Fig. 5.5 we have simulated the linear response of a chain of five spherical MNPs of LSMO35 in water. There is a further redshift from the single MNP Debye compared to the two MNP case (Fig. 5.4) for the magnetic susceptibility. Fig. 5.5 is a low fidelity simulation and Fig. 5.6 is a high fidelity simulation of the same system. From a peak frequency of $1/\tau_B$ rad s$^{-1}$ ($5.24 \times 10^4$ Hz) for the single MNP Debye model there is a redshift to $3.281(2) \times 10^{-2}/\tau_B$ rad s$^{-1}$ ($1.718(1) \times 10^3$ Hz) for the five MNP chain.

Unlike the two MNP case the magnetic susceptibility deviates from a purely rotational description (a re-fitted Debye model) at high frequencies. The separation of the peak and the shoulder by more than 2 orders of magnitude in frequency enables the separation of the features by the application of the Kabsch algorithm as seen in pane (b) of Fig. 5.5, and more clearly in the high fidelity simulation in pane (b) of Fig. 5.6. In particular, at very high frequency the MNPs respond independently (incoherently) while at lower frequency they respond collectively (coherently). The independent (coherent) response matches the single MNP Debye model as expected.

The shoulder (indicated by the arrow in Figs. 5.5 and 5.6) in the aligned and total magnetic susceptibility denotes a change back to a single MNP analytical Debye susceptibility as can be seen more clearly in Fig. 5.6.
Figure 5.5: Five MNP chain, Low fidelity, T=300 K Radius=10 nm, $\tau_B = 3.039 \mu$s, (a) MDOS (b) Magnetic Susceptibility. The ‘Debye’ curve is the analytical Debye equation for a single MNP (Eqn 3.33). The ‘Fit’ is a plot of the fitting equation using Eqn 5.1 as described in Section 5.2.2. The hashed region is the region where the fit was calculated. ‘Total’ is the MDOS and magnetic susceptibility from the simulation. ‘Aligned’ and ‘Rotational’ are calculated from the Kabsch algorithm (Section 3.3.3.3). The grey region is the error bars associated with the 96 statistical repetitions. ‘Equivalent ellipsoid’ is the analytical ellipsoidal approximation (Section 3.3.1.1). The arrow is to show the area where the dynamics return to that of a single MNP.

The shoulder starts forming at $\omega \tau_B = 10$ before peaking at $\omega \tau_B = 10^2$. The slight increase at the tail of the data is an artefact of the simulation. Our fit shows that there are two distinct regions of note (fitting values can be seen in Table 5.3). A return to single MNP dynamics is picked up by the aligned MDOS and magnetic susceptibility. The Debye like chain dynamics are qualitatively the same as the ellipsoidal relaxation is picked up in the rotational MDOS.
Figure 5.6: Five MNP chain, High fidelity, T=300 K Radius=10 nm, $\tau_B=3.039 \mu$s, (a) MDOS (b) Magnetic Susceptibility. The ‘Debye’ curve is the analytical Debye equation for a single MNP (Eqn 3.33). The ‘Fit’ uses the fitting parameters from Fig. 5.5. The hashed region is the region where the fit was calculated. ‘Total’ is the MDOS and magnetic susceptibility from the simulation. ‘Aligned’ and ‘Rotational’ are calculated from the Kabsch algorithm (Section 3.3.3.3). The grey region is the error bars associated with the 96 statistical repetitions. ‘Equivalent ellipsoid’ is the analytical ellipsoidal approximation (Section 3.3.1.1). The arrow is to show the area where the dynamics return to that of a single MNP.

The ellipsoidal approximation in Figs. 5.5 and 5.6 is no longer close to the total magnetic susceptibility. The ‘Rotational’ magnetic susceptibility predicts the same low frequency dynamics as the ellipsoidal approximation. As the frequency increases interparticle effects change the dynamics due to the chain no longer being perfectly straight. Table 5.4 shows the nearest neighbour distances between MNPs. Although the MNPs are not overlapping (the centres of the first nearest neighbours are separated by more than an MNP diameter) there is a definite bend in the chain noted by the fact that nearest neighbour average distances are lower than the nominal distance for a straight chain for second nearest neighbours onwards. The bend of the chain can be seen clearly in pane b) of Fig. C.1. The bending of the chain makes the ellipsoidal relaxation estimation of
the relaxation less valid as the estimation is based on a standard ellipsoid.

In Fig. 5.7 we have simulated the linear response of a chain of ten spherical MNPs of LSMO35 in water. Fig. 5.7 is a low fidelity simulation and Fig. 5.8 is a high fidelity simulation of the same system. There are many of the same features present that were seen in Fig. 5.5.

![Graph](image)

Figure 5.7: Ten MNP chain, Low fidelity, T=300 K Radius=10 nm, $\tau_B=3.039 \mu s$, (a) MDOS (b) Magnetic Susceptibility. The ‘Debye’ curve is the analytical Debye equation for a single MNP (Eqn 3.33). The ‘Fit’ is a plot of the fitting equation using Eqn 5.1 as described in Section 5.2.2. The hashed regions are the regions where the fit was calculated. ‘Total’ is the MDOS and magnetic susceptibility from the simulation. ‘Aligned’ and ‘Rotational’ are calculated from the Kabsch algorithm (Section 3.3.3.3). The grey region is the error bars associated with the 96 statistical repetitions. ‘Equivalent ellipsoid’ is the analytical ellipsoidal approximation (Section 3.3.1.1). The arrow is to show the area where the dynamics return to that of a single MNP.

The redshift of the peak of the total and rotational magnetic susceptibilities now at $7.32(1) \times 10^{-3}/\tau_B \text{ rad s}^{-1}$ ($3.833(7) \times 10^2 \text{ Hz}$) has moved further from the single MNP Debye model peak at $5.24 \times 10^4 \text{ Hz}$. From the fitting of the rotational magnetic susceptibility the relaxation time, $\tau_B$ is $4.152(8) \times 10^{-4} \text{ s}$ compared to the analytical value.
of $3.04 \times 10^{-6}$ s.

Figure 5.8: Ten MNP chain, High fidelity, T=300 K Radius=10 nm, $\tau_B=3.039$ µs, (a) MDOS (b) Magnetic Susceptibility. The ‘Debye’ curve is the analytical Debye equation for a single MNP (Eqn 3.33). The ‘Fit’ uses the fitting parameters from Fig. 5.7. The hashed regions are the regions where the fit was calculated. ‘Total’ is the MDOS and magnetic susceptibility from the simulation. ‘Aligned’ and ‘Rotational’ are calculated from the Kabsch algorithm (Section 3.3.3.3). The grey region is the error bars associated with the 96 statistical repetitions. ‘Equivalent ellipsoid’ is the analytical ellipsoidal approximation (Section 3.3.1.1). The arrow is to show the area where the dynamics return to that of a single MNP.

The shoulder that was visible in the five MNP case where the MNP dynamics return to the single MNP magnetic susceptibility is also visible in the ten MNP simulation. The analytical ellipsoidal fit has also moved further from the rotational MDOS as the chain becomes more flexible with increasing length as seen in Table 5.4.

Formation of the shoulder is at the same frequency as the five MNP shoulder ($\omega \tau_B = 10$) leading to a peak again at $\omega \tau_B = 10^2$. The shoulder shows the dynamics of the chain are returning to the same as a single MNP for higher frequencies independent of the number of MNPs in the chain. The shoulder and the Debye peak are no longer fitted
across a continuous range as seen in the five MNP case. From the fit of the $\tau_B$ for the 10 MNP case, the ratio between the propagation time and the rotational relaxation time is 17.3 and is approaching 10 (see Table 5.2) where convergence is less assured as was discussed in Section 3.3.3.2.

In Fig. 5.9 we have simulated the linear response of a chain of twenty spherical MNPs of LSMO35 in water. Fig. 5.9 is a low fidelity simulation and Fig. 5.10 is a high fidelity simulation of the same system. Continuing the trend set by previous chain extensions there is a larger redshift of the peak of the magnetic susceptibility with a peak shift from the Debye peak frequency of $5.24 \times 10^4$ Hz to a peak frequency of $3.55(9) \times 10^{-3}/\tau_B \text{ rad s}^{-1} (1.599(5) \times 10^2 \text{ Hz})$.

![Figure 5.9: Twenty MNP chain, Low fidelity, T=300 K Radius=10 nm, $\tau_B=3.039 \mu$s, (a) MDOS (b) Magnetic Susceptibility. The ‘Debye’ curve is the analytical Debye equation for a single MNP (Eqn 3.33). The ‘Fit’ is a plot of the fitting equation using Eqn 5.1 as described in Section 5.2.2. The hashed regions are the regions where the fit was calculated. ‘Total’ is the MDOS and magnetic susceptibility from the simulation. ‘Aligned’ and ‘Rotational’ are calculated from the Kabsch algorithm (Section 3.3.3.3). The grey region is the error bars associated with the 96 statistical repetitions. ‘Equivalent ellipsoid’ is the analytical ellipsoidal approximation (Section 3.3.1.1). The arrow is to show the area where the dynamics return to that of a single MNP.](image-url)
The lowest frequencies that are captured by the simulation do not completely capture the peak of the magnetic susceptibility. This is consistent with the calculated value of $N_{\text{mag,corr}}$ of 7.24 (see Table 5.2) which is less than the desired $10N_{\text{mag,corr}}$ as was discussed in Section 5.2.2. A side effect of the missing peak is the fit of the low frequency is less accurate although there is no effect on the higher frequency fitting of the shoulder.

Figure 5.10: Twenty MNP chain, High fidelity, $T=300$ K, Radius=10 nm, $\tau_B=3.039$ µs, (a) MDOS (b) Magnetic Susceptibility. The ‘Debye’ curve is the analytical Debye equation for a single MNP (Eqn 3.33). The ‘Fit’ uses the fitting parameters from Fig. 5.9. The hashed regions are the regions where the fit was calculated. ‘Total’ is the MDOS and magnetic susceptibility from the simulation. ‘Aligned’ and ‘Rotational’ are calculated from the Kabsch algorithm (Section 3.3.3.3). The grey region is the error bars associated with the 96 statistical repetitions. ‘Equivalent ellipsoid’ is the analytical ellipsoidal approximation (Section 3.3.1.1). The arrow is to show the area where the dynamics return to that of a single MNP.

As with 5 and 10 MNP chains the peak frequency of the 20 MNP shoulder is at $\omega\tau_B = 10^2$ which suggests its invariant with chain length. The ellipsoidal approximation is again qualitatively equal to the rotational MDOS. As Table 5.4 shows the distance between nearest neighbour pairs of the 20 MNP chain is on average less than the nominal distance for a straight chain. The ends of the chain are nearly as close as the
average fifth nearest neighbour.

The separation of the fit parameters required has now increased to a full order of magnitude which is consistent with \( N_{\text{mag,corr}} \) for the 20 MNP chain which is now less than 10 as seen in Table 5.2.

Notable values for the different chain lengths of the LSMO35 MNP chains with a 10 nm radius can be seen in Table 5.3. Measuring the first nearest neighbour distances of all the chains as shown in Table 5.4 shows that the interparticle distances are always slightly greater than the diameter of each MNP.

Table 5.4: Nearest Neighbour distances for the 10 nm radius MNPs, measured from the centre of the MNPs

<table>
<thead>
<tr>
<th>Chain Length (nm)</th>
<th>2</th>
<th>5</th>
<th>10</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>( N )</td>
<td>Straight</td>
<td>2</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>1</td>
<td>2 ( \times 10^1 )</td>
<td>2.020(2) ( \times 10^1 )</td>
<td>2.018(2) ( \times 10^1 )</td>
<td>2.018(2) ( \times 10^1 )</td>
</tr>
<tr>
<td>2</td>
<td>4 ( \times 10^1 )</td>
<td>–</td>
<td>3.93(1) ( \times 10^1 )</td>
<td>3.91(1) ( \times 10^1 )</td>
</tr>
<tr>
<td>3</td>
<td>6 ( \times 10^1 )</td>
<td>–</td>
<td>5.72(6) ( \times 10^1 )</td>
<td>5.63(3) ( \times 10^1 )</td>
</tr>
<tr>
<td>4</td>
<td>8 ( \times 10^1 )</td>
<td>–</td>
<td>7.4(1) ( \times 10^1 )</td>
<td>7.15(8) ( \times 10^1 )</td>
</tr>
<tr>
<td>5</td>
<td>1 ( \times 10^2 )</td>
<td>–</td>
<td>–</td>
<td>8.4(1) ( \times 10^2 )</td>
</tr>
<tr>
<td>7</td>
<td>1.4 ( \times 10^2 )</td>
<td>–</td>
<td>–</td>
<td>1.03(4) ( \times 10^2 )</td>
</tr>
<tr>
<td>9</td>
<td>1.8 ( \times 10^2 )</td>
<td>–</td>
<td>–</td>
<td>1.14(6) ( \times 10^2 )</td>
</tr>
<tr>
<td>12</td>
<td>2.4 ( \times 10^2 )</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>16</td>
<td>3.2 ( \times 10^2 )</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>19</td>
<td>3.8 ( \times 10^2 )</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

The list of pairs is the average of all pairs for instance 1 is every nearest neighbour and 2 is every second nearest neighbour etc.

As the distance between the pairs increases with second and third nearest neighbours the average separation is not a multiple of the diameter of a single MNP. If the chain was perfectly straight the nearest neighbour distances would scale linearly as a multiple of the diameter of a single MNP. The distance between nearest neighbour pairs is slowly decreasing per MNP from 20.2 nm for the first nearest neighbour pair to an average of 18.5 nm for the fourth nearest neighbour pairs for a five MNP string showing that the chain is flexible and not perfectly straight. The ten and twenty MNP chains increase again in flexibility as distances reduce further between nearest neighbour pairs. The flexibility of the chains can be seen in Appendix C where it is very apparent the chains do not stay straight for LSMO35 chains.
5.2. Chains

5.2.3.2 20 nm Radius

For these larger MNP of LSMO35 we are around our limit of $10N_{\text{mag,corr}}$ as Table 5.5 shows. Therefore the low frequency end of the figures in this section are at the limit of statistical accuracy.

Table 5.5: The number of correlation times for each low fidelity simulation for 20 nm radius MNPs

<table>
<thead>
<tr>
<th>MNP</th>
<th>20 nm</th>
<th>20 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>Time [s]</td>
<td>$\tau_B$ (fit) [s]</td>
</tr>
<tr>
<td>1 (exact)</td>
<td>$7.2 \times 10^{-3}$</td>
<td>$2.43 \times 10^{-5}$</td>
</tr>
<tr>
<td>5</td>
<td>$7.2 \times 10^{-3}$</td>
<td>$5.641(3) \times 10^{-4}$</td>
</tr>
<tr>
<td>10</td>
<td>$7.2 \times 10^{-3}$</td>
<td>$1.128(1) \times 10^{-3}$</td>
</tr>
</tbody>
</table>

The larger 20 nm MNPs form much stiffer chains that are less prone to bending than the smaller 10 nm MNPs as the nominal distance between pairs is closer to the value for a straight chain as Table 5.6 shows. This is can also be clearly seen when comparing the ten MNP chains in Figs. 5.14 and C.2.

20 nm MNPs have an 8 times larger volume due to the radius being double the 10 nm MNPs suggesting that the frequency at which the MNPs oscillate individually is radius and volume dependent.

Table 5.6: Nearest Neighbour distances for the 20 nm radius MNPs, measured from the centre of the MNPs

<table>
<thead>
<tr>
<th>Chain Length (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N$</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>2</td>
</tr>
<tr>
<td>3</td>
</tr>
<tr>
<td>4</td>
</tr>
<tr>
<td>5</td>
</tr>
<tr>
<td>7</td>
</tr>
<tr>
<td>9</td>
</tr>
</tbody>
</table>

The list of pairs is the average of all pairs for instance 1 is every nearest neighbour and 2 is every second nearest neighbour etc.

Similar trends that were seen in the smaller 10 nm radius MNPs continue for 20 nm radius MNPs such as a redshift in the turning point of the magnetic susceptibility as can be seen in Table 5.7.
The frequency shift shown below in Fig. 5.11 for the five MNP chain is from a single MNP Debye peak frequency of \(1/\tau_B \text{rad s}^{-1}\) (equating to \(2.58 \times 10^5 \text{Hz}\)) to a peak of \(4.310(3) \times 10^{-2}/\tau_B \text{rad s}^{-1}\) (\(2.821(2) \times 10^2 \text{Hz}\)). Fig. 5.11 is a low fidelity simulation of the five MNP chain and Fig. 5.12 is a high fidelity simulation of the same system.

The shoulder that is visible in Fig. 5.5 at \(\omega \tau_B = 10^2\) is shifted for the 20 nm MNP case to \(\omega \tau_B = 10^3\) as seen in Fig. 5.11. A higher frequency oscillation is needed for each MNP to act independently of the chain as is seen in Fig. 5.12.

![Figure 5.11: Five MNP chain, Low fidelity, T=300 K Radius=20 nm, \(\tau_B=24.3 \mu\text{s}\), (a) MDOS (b) Magnetic Susceptibility. The ‘Debye’ curve is the analytical Debye equation for a single MNP (Eqn 3.33). The ‘Fit’ is a plot of the fitting equation using Eqn 5.1 as described in Section 5.2.2. The hashed regions are the regions where the fit was calculated. ‘Total’ is the MDOS and magnetic susceptibility from the simulation. ‘Aligned’ and ‘Rotational’ are calculated from the Kabsch algorithm (Section 3.3.3.3). The grey region is the error bars associated with the 96 statistical repetitions. ‘Equivalent ellipsoid’ is the analytical ellipsoidal approximation (Section 3.3.1.1). The arrow is to show the area where the dynamics return to that of a single MNP.](image-url)
Figure 5.12: Five MNP chain, High fidelity, T=300 K Radius=20 nm, $\tau_B=24.3$ µs, (a) MDOS (b) Magnetic Susceptibility. The ‘Debye’ curve is the analytical Debye equation for a single MNP (Eqn 3.33). The ‘Fit’ uses the fitting parameters from Fig. 5.11. The hashed regions are the regions where the fit was calculated. ‘Total’ is the MDOS and magnetic susceptibility from the simulation. ‘Aligned’ and ‘Rotational’ are calculated from the Kabsch algorithm (Section 3.3.3.3). The grey region is the error bars associated with the 96 statistical repetitions. ‘Equivalent ellipsoid’ is the analytical ellipsoidal approximation (Section 3.3.1.1). The arrow is to show the area where the dynamics return to that of a single MNP.

The estimate of the ellipsoid relaxation is closer to that of our fit of the larger MNPs relaxation. For comparison the 10 nm radius 5 MNP chain has a $\tau_r$ 4 times smaller than our fit however the larger 20 nm MNPs have a $\tau_r$ fit that is 2.5 times smaller than our fit.
5.2. Chains

Table 5.7: $\chi_{c,0}$, $\tau_B$ (fit) and $\tau_r$, for different chain lengths of 20 nm MNPs

<table>
<thead>
<tr>
<th>MNP</th>
<th>20 nm</th>
<th>20 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N$</td>
<td>$\chi_{c,0}$</td>
<td>$\tau_r$</td>
</tr>
<tr>
<td>1(exact)</td>
<td>9.52$\cdot10^1$</td>
<td>2.43$\cdot10^{-5}$</td>
</tr>
<tr>
<td>5</td>
<td>3.58$\cdot10^2$</td>
<td>1.97$\cdot10^{-4}$</td>
</tr>
<tr>
<td>10</td>
<td>5.07$\cdot10^2$</td>
<td>4.51$\cdot10^{-4}$</td>
</tr>
</tbody>
</table>

The fit limits are the data ranges used to fit $\tau_B$ (fit) in units of $\tau_B$ for a single MNP calculated using Eqn 2.10.

The trend continues for 10 MNP chains where for the 10 nm MNPs $\tau_r$ is 8 times smaller than our fit whereas for 20 nm MNPs it is only 3 times smaller. There is obviously still quite a large difference between $\tau_r$ and $\tau_B$ (fit) but it seems to be now more closely related to variations in the overall chain length as was seen with the two MNP chain with a 10 nm radius.

In Fig. 5.13 we can see a ten MNP chain of 20 nm MNPs. The simulation is at the limit of $N_{\text{mag,corr}}$ as seen in Table 5.5, reducing the accuracy of the lower frequency data. The fit parameters required to reasonably fit the magnetic susceptibility are within an order of magnitude as can be seen in Table 5.7. The frequency shift for the 10 MNP chain is from a Debye peak frequency of $2.58 \times 10^5$ Hz to a peak of $2.154(6) \times 10^{-2}/\tau_B$ rad s$^{-1}$ (1.410(2) $\times 10^2$ Hz).
Figure 5.13: Ten MNP chain, Low fidelity, T=300 K Radius=20 nm, $\tau_B=24.3$ µs, (a) MDOS (b) Magnetic Susceptibility. The ‘Debye’ curve is the analytical Debye equation for a single MNP (Eqn 3.33). The ‘Fit’ is a plot of the fitting equation using Eqn 5.1 as described in Section 5.2.2. The hashed regions are the regions where the fit was calculated. ‘Total’ is the MDOS and magnetic susceptibility from the simulation. ‘Aligned’ and ‘Rotational’ are calculated from the Kabsch algorithm (Section 3.3.3.3). The grey region is the error bars associated with the 96 statistical repetitions. ‘Equivalent ellipsoid’ is the analytical ellipsoidal approximation (Section 3.3.1.1). The arrow is to show the area where the dynamics return to that of a single MNP.

Finally the high frequency simulation of a chain of ten 20 nm radius MNPs in Fig. 5.14 shows a very good agreement with the single MNP Debye model above $\omega \tau_B = 10^3$ as was also seen for the five MNP chain in Fig. 5.12. As with the smaller MNPs the frequency at which there is a return to single MNP dynamics seems to be invariant with chain length. The interparticle motion of the chain shown by the aligned MDOS again can be seen to be the driving force of the return to single MNP dynamics.
The dynamics of 20 nm radius LSMO35 MNPs is very similar to that of the 10 nm radius LSMO35 MNPs. The major difference is the frequency at which the dynamics of the chains return to single MNP dynamics with an absolute frequency increase of ~25% from 32.89 MHz for 10 nm radius LSMO35 MNPs to 41.15 MHz for 20 nm radius LSMO35 MNPs. Further simulations would need to be conducted on larger MNP to find a trend of the frequency increase unfortunately this is not possible with current simulation limitations. For smaller MNP, effects of Néel relaxations should not be ignored as we approach sub nanometre scale, sizes which LSMO has not been synthesised at.
5.2. Chains

5.2.4 LSMO40

We modelled two chains of LSMO40, 5 and 10 MNP chains. The magnetic moment of LSMO40 MNPs is much less than that of LSMO35 MNPs therefore the initial chain did not stay magnetically bound in a simulated water solution and dispersed into a small agglomerate. We are therefore well within our $N_{\text{mag,corr}}$ rule of thumb as Table 5.8 shows.

Table 5.8: The number of correlation times for each low fidelity simulation for 10 nm radius MNPs

<table>
<thead>
<tr>
<th>MNP</th>
<th>Time [s]</th>
<th>$\tau_B$(fit) [s]</th>
<th>$N_{\text{mag,corr}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (exact)</td>
<td>7.2 x 10^{-3}</td>
<td>3.04 x 10^{-6}</td>
<td>2.37 x 10^3</td>
</tr>
<tr>
<td>5</td>
<td>7.2 x 10^{-3}</td>
<td>3.05(1) x 10^{-4}</td>
<td>2.36 x 10^3</td>
</tr>
<tr>
<td>10</td>
<td>7.2 x 10^{-3}</td>
<td>3.05(2) x 10^{-3}</td>
<td>2.36 x 10^3</td>
</tr>
</tbody>
</table>

This is further confirmed by the calculation for both the 5 and 10 MNP $\chi_{c,0}$ equal to $\chi_0$ for a single LSMO40 MNP.

Table 5.9: $\chi_{c,0}$ and $\tau_B$(fit), for different chain lengths of 10 nm MNPs

| MNP | $\chi_{c,0}$ | $\tau_B$(fit) [s] & Fit Limits |
|-----|-------------|----------------|------------------|
| 1(exact) | 8.71 x 10^{1} | 2.43 x 10^{-5} & - |
| 5    | 8.71 x 10^{2} | 3.05(1) x 10^{-4} & [2, 30] |
| 10   | 8.71 x 10^{2} | 3.05(2) x 10^{-3} & [2, 30] |

The fit limits are the data ranges used to fit $\tau_B$(fit) in units of $\tau_B$ for a single MNP calculated using Eqn 2.10.

As Fig. 5.15 shows the simulation of 5 LSMO40 MNP chain acts completely differently from LSMO35 chains. However the analytical Debye MDOS matches perfectly with the total and aligned MDOS of the simulation.

As the aligned is designed to pick up the individual MNP dynamics it is assured that the MNPs have dispersed into an agglomerate. This is confirmed by the second frame of Fig. C.6.
Figure 5.15: Five MNP chain, Low fidelity, T=300 K Radius=10 nm, $\tau_B=3.039 \mu$s. (a) MDOS (b) Magnetic Susceptibility. The ‘Debye’ curve is the analytical Debye equation for a single MNP (Eqn 3.33). The ‘Fit’ is the Debye curve using $\tau_B = \tau_B(\text{fit})$ as described in Section 5.2.2. The hashed region is the region where the fit was calculated. ‘Total’ is the MDOS and magnetic susceptibility from the simulation. ‘Aligned’ and ‘Rotational’ are calculated from the Kabsch algorithm (Section 3.3.3.3). The grey region is the error bars associated with the 96 statistical repetitions.

The rotational magnetic susceptibility is dependent on frequency and picks up the dynamics of the whole agglomerate. The shape suggests that at very low frequencies the agglomerate will act like a large single MNP although due to the limits of our simulations this cannot be proven.

The same dynamics are mirrored in Fig. 5.16 where the aligned and total magnetic susceptibility follow the analytical Debye model for a single MNP. The number of MNPs has not increased the magnetic susceptibility of the MNP system therefore the SAR of each MNP is lower.
5.3. Summary of simulations and calculation of the specific absorption rate

We have conducted a varied array of statistically relevant simulations examining the dynamics of LSMO MNPs. These are listed below in Table 5.10.

The MNP do not stay as a chain due to the smaller magnetic moment of the LSMO40 compared to the LSMO35 MNP. In a more viscous fluid the magnetic moment may be larger enough to increase the force needed to separate the MNPs.

5.3 Summary of simulations and calculation of the specific absorption rate

We have conducted a varied array of statistically relevant simulations examining the dynamics of LSMO MNPs. These are listed below in Table 5.10.
We have found that chains of MNPs do not have the same dynamics as either an ellipsoid with the same dimensions or a single MNP. To be able to compare the simulations to physical experiments a measurable quantity is needed. As discussed in Section 3.3.2 the SAR is accessible through experiments. Using the same values of magnetic field amplitude (137.6 Oe) and frequency of \(1.09 \times 10^6\) rad s\(^{-1}\), and the properties of LSMO35 used in Eqn 3.42 the SAR has been calculated using \(\tau_B(\text{fit})\) of the simulated chains in Table 5.11.

### Table 5.11: The Specific Absorption rate of chains of LSMO35 MNPs

<table>
<thead>
<tr>
<th>MNP</th>
<th>SAR per MNP [W g(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10 nm</td>
</tr>
<tr>
<td>N</td>
<td>Low fidelity</td>
</tr>
<tr>
<td>1</td>
<td>4.618 \times 10^2</td>
</tr>
<tr>
<td>2</td>
<td>4.793 \times 10^2</td>
</tr>
<tr>
<td>5</td>
<td>1.608 \times 10^2</td>
</tr>
<tr>
<td>10</td>
<td>1.847 \times 10^1</td>
</tr>
<tr>
<td>20</td>
<td>9.092</td>
</tr>
</tbody>
</table>

With the LSMO40 MNP the SAR is as expected lower than a single LSMO35 MNP and therefore as all simulations relaxed into small agglomerates the same is true for the 5 and 10 LSMO40 MNP simulations.

### Table 5.12: The Specific Absorption rate of LSMO40 MNPs

<table>
<thead>
<tr>
<th>MNP</th>
<th>SAR per MNP [W g(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>10 nm</td>
</tr>
<tr>
<td>1(exact)</td>
<td>1.501 \times 10^2</td>
</tr>
<tr>
<td>5</td>
<td>3.501 \times 10^1</td>
</tr>
<tr>
<td>10</td>
<td>1.250 \times 10^1</td>
</tr>
</tbody>
</table>
This chapter thus makes very specific predictions for LSMO35 and LSMO40 MNPs. The only comparison that can be made is to bulk systems of LSMO where the SAR was recorded by McBride et al. (2016) as \(45 - 60 \text{ W g}^{-1}\) for LSMO35 and for LSMO40 where the SAR was recorded as \(35 - 50 \text{ W g}^{-1}\) [26]. Further work, beyond the extent to this thesis, is required to perform experimental results to confirm these results for such small numbers of MNP.
Chapter 6

Conclusion

In this thesis we have studied the dynamics of clusters and chains of MNPs in solution, specifically in our case water. In particular we have focused on chains of MNPs that form through the spontaneous agglomeration of clusters. Chains of MNPs have a complex behaviour that cannot be simply described by the use of the Debye model for singular spherical MNPs or the Perrin model for singular ellipsoidal MNPs [13, 63].

In Chapter 3, a detailed explanation of the methods and algorithms used in simulating MNPs were shown. The simulation of magnetic nanoparticles was analysed by separating the simulation into translational and rotational motion. From the equations of Langevin dynamics for rotational Brownian motion it was shown that in the limit of large damping the translational and rotational motion can be modelled by the same stochastic Landau-Lifshitz-Gilbert equation. The translational and rotational motion dynamics were implemented using an extended position Verlet integration. A splitting scheme was shown to add stability to the integrator. The position Verlet was further split to accommodate the implicit midpoint method for calculating the rotation of the magnetisation of the system. Separation of resonant frequencies of the magnetic susceptibility of chains of magnetic nanoparticles was undertaken using the Kabsch algorithm.

In Chapter 4, details of the numerical implementation and design of the model was demonstrated. The design of the program, named Mango, has enabled the production of results on parallel supercomputers using four nodes of twenty-four cores. Mango is able to generate an ensemble trajectory of a system of MNPs with user definable magnetic and translational potentials. For a user, Mango is designed to be easy to set up and use and to be included as part of larger data processing efforts. Built
in data processing capabilities include autocorrelation function calculations to obtain magnetic susceptibility from a trajectory. Optimisations of the implementation have allowed for millisecond timescales to be simulated feasibly on existing infrastructure. An ensemble of ninety-six trajectories of magnetic nanoparticle chains of up to twenty particles in length were simulated on ninety-six cores in parallel. Scaling tests have shown that the design is an efficient simulation system and scales more efficiently than implemented examples of similar algorithms such as the Suzuki–Trotter decomposition used by LAMMPS [178].

Chapter 5 shows the results of simulations of clusters and chains of MNPs. Single MNP simulations show consistency with the analytical Debye model of MNPs. A chain of MNPs has the same high frequency magnetic response as a single Debye particle. While qualitatively the theoretical magnetic susceptibility of an ellipsoid was the same as the fit of the data in the low frequency regime, there was a shift to lower frequencies from the ellipsoidal magnetic susceptibility to the simulated chain.

In all the LSMO35 chain susceptibilities, we have observed a smooth cross-over between the chain of particles acting as a complete chain to acting as an individual particle. At higher frequencies there is no time for the chain to respond as a whole. While at lower frequencies the MNP chain responds as a rigid body. The cross-over is not dependent on the chain length as seen for 10 nm and 20 nm radius particles in Sections 5.2.3.1 and 5.2.3.2. The cross-over frequency is always at \( \sim 3.3 \times 10^7 \text{ rad s}^{-1} \) for 10 nm MNP chains and at \( \sim 3.9 \times 10^8 \text{ rad s}^{-1} \) for 20 nm MNP chains. However, the cross-over frequency increases as radius increases.

LSMO40 MNPs are less magnetic than LSMO35 MNPs this led to the separation of LSMO40 chains into mono dispersed clusters. Unlike the lower strontium dopant counterpart the coalescing of MNP was not observed due to the weaker magnetisation on the MNPs.

We have shown that there are at least two resonant frequency modes within LSMO35 MNP chains. The Kabsch algorithm discussed in Section 3.3.3.3 only enables separation of resonant frequency modes when there is a large separation between the frequencies of these two modes. In addition to these two main features, further resonant modes corresponding to normal modes of the LSMO35 MNP chains are expected. However, due to their large superposition with the main Debye peak, it was not possible to resolve them accurately. A larger statistical sampling, not necessary for the achievement of the main objectives of this work, may shed more light on the interparticle motion of the chains.

The Kabsch algorithm has also allowed for the separation of single MNP dynamics of
LSMO40 MNPs from the agglomerate motion. The mono dispersed agglomerate seems to act to some extent as a single body at low frequencies although the dynamics are not fully captured by our simulations. To explore this fully longer simulations than are currently possible would need to be conducted to examine these lower frequencies.

The specific absorption rate (SAR) of LSMO35 MNP chains is greatly reduced as the chain length increases as summarised in Table 5.11. For a 10 nm chain of LSMO35 the SAR reduces from $4.793 \times 10^2 \text{W g}^{-1}$ for a single MNP to $9.092 \text{W g}^{-1}$ per MNP for a twenty MNP chain. The SAR of LSMO40 also is reduced compared to a single MNP from a value of $1.501 \times 10^2 \text{W g}^{-1}$ for a single MNP to $1.250 \times 10^1 \text{W g}^{-1}$ per MNP for a ten MNP agglomerate. This is an important quantification of the effect of MNP aggregation of the RF heat generation using MNP solutions. These numerical findings can in principle be validated experimentally, although this validation has not been attempted as a part of this work. We can only mention an indirect confirmation from the work of McBride et al. (2017) that has shown a reduced SAR in the case of crystallised LSMO35 where the SAR of the sample was recorded between $1.18 \times 10^1 \text{W g}^{-1}$ to $4.11 \times 10^1 \text{W g}^{-1}$ [23]. A similar indirect confirmation can be seen for LSMO40 where the SAR of crystallised LSMO40 is $35 \text{W g}^{-1}$ to $50 \text{W g}^{-1}$ [26].

In summary, we have shown that the formation of MNP chains has a large impact on the magnetic susceptibility of a MNP system and the corresponding SAR. The agglomeration of MNPs into chains is a process that cannot be neglected because the response of a chain of MNPs is not the same as non-interacting MNPs. The computer program, Mango, developed during this project may be also used to investigate the next level of MNP aggregation in solutions, namely chain aggregation in larger clusters.

### 6.1 Future work

In future work it would be particularly interesting to investigate whether the two main spectral features of the chains will be still recognisable in a larger MNP cluster consisting of multiple chains of MNP. It would also be interesting to include Néel relaxations in simulations of smaller MNP to model the effect of the extra dynamics of the relaxation. Furthermore the eventual aim should be the simulation of bulk material consisting of MNPs as is currently explored experimentally. However, further optimisation of the code is needed in order to scale up to the appropriate cluster size.

In future work on the program further parallelisation should be undertaken beyond the current embarrassingly parallel construction to utilise the ever increasing processor count available on supercomputing clusters. This would involve parallelising the magnetic and translational potentials to allow for interactions in a system to be calculated
6.1. Future work

independently where possible. To be able to model MNPs in low friction environments rotational magnetic potentials would need to be added to the program. Inclusion of more complex potentials such as the DLVO potential would allow for the modelling of more complex translational interactions making it possible to more accurately simulate physical systems.
Appendix A

Default Input File

Below is a full input file for the Mango program as discussed in Section 4.1.1.

<table>
<thead>
<tr>
<th># Input files</th>
<th></th>
<th># Input file location</th>
</tr>
</thead>
<tbody>
<tr>
<td>InputFile</td>
<td>None</td>
<td></td>
</tr>
<tr>
<td>RestartFile</td>
<td>None</td>
<td># Restart file location</td>
</tr>
<tr>
<td>PositionFile</td>
<td>None</td>
<td># Positions file location</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th># Properties</th>
<th></th>
<th># External Field Frequency [Hz]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ExternalFieldFreq</td>
<td>1e-6</td>
<td></td>
</tr>
<tr>
<td>ExternalFieldStrength</td>
<td>167.0</td>
<td># External Field Strength [1e-6 Gauss]</td>
</tr>
<tr>
<td>MediumViscosity</td>
<td>0.01002</td>
<td># Solvent Viscosity [g/(cm *s)]</td>
</tr>
<tr>
<td>MagneticDensity</td>
<td>85</td>
<td># Magnetic Density of particles [emu/g]</td>
</tr>
<tr>
<td>ParticleDensity</td>
<td>6.99</td>
<td># Density of each particle [g /cm³]</td>
</tr>
<tr>
<td>ParticleRadius</td>
<td>5.0</td>
<td># Radius of each particle [1e-6cm]</td>
</tr>
<tr>
<td>Temperature</td>
<td>298.0</td>
<td># Temperature [K]</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th># Calculation Options</th>
<th></th>
<th># Background Noise switch</th>
</tr>
</thead>
<tbody>
<tr>
<td>BackgroundNoise</td>
<td>True</td>
<td></td>
</tr>
<tr>
<td>Boxxize</td>
<td>50</td>
<td># Periodic boundary box size [1e-6cm]</td>
</tr>
<tr>
<td>Epsilon</td>
<td>None</td>
<td># Set depth of Potential Well</td>
</tr>
<tr>
<td>Iterations</td>
<td>400.0</td>
<td># Number of Iterations</td>
</tr>
<tr>
<td>Labview</td>
<td>True</td>
<td># Remove initial cluster momentum</td>
</tr>
<tr>
<td>MagnetisationSW</td>
<td>True</td>
<td># Magnetisation calculation switch</td>
</tr>
<tr>
<td>NumberParticles</td>
<td>5</td>
<td># Number of Particles</td>
</tr>
<tr>
<td>Optimisation</td>
<td>False</td>
<td># Auto-minimise energy of the system</td>
</tr>
<tr>
<td>PeriodicBoundaries</td>
<td>True</td>
<td># Periodic Boundary Conditions</td>
</tr>
<tr>
<td>Potential</td>
<td>False</td>
<td># Change potential used</td>
</tr>
<tr>
<td>Repetitions</td>
<td>10</td>
<td># Number of statistical repetitions</td>
</tr>
<tr>
<td>SkipSave</td>
<td>1</td>
<td># Save every # iterations</td>
</tr>
<tr>
<td>SusceptibilityCalc</td>
<td>False</td>
<td># Zero field Calculation</td>
</tr>
<tr>
<td>ThermalOptim</td>
<td>False</td>
<td># Thermally optimise initial conditions</td>
</tr>
<tr>
<td>Timestep</td>
<td>20</td>
<td># Timestep [ps]</td>
</tr>
</tbody>
</table>
# Postprocessing

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Align</td>
<td>False</td>
<td># Align with Kabsch algorithm</td>
</tr>
<tr>
<td>Blocking</td>
<td>5, 10, 20, 50, 100</td>
<td># Block averaging bins</td>
</tr>
<tr>
<td>CreateFile</td>
<td>False</td>
<td># Create output files</td>
</tr>
<tr>
<td>Equilibrate</td>
<td>0.1</td>
<td># Equilibration fraction of trajectory</td>
</tr>
<tr>
<td>PlotColumns</td>
<td>False</td>
<td># Plot simple datasets</td>
</tr>
<tr>
<td>Run</td>
<td>False</td>
<td># Select run number</td>
</tr>
<tr>
<td>KineticTemp</td>
<td>False</td>
<td># Calculate kinetic temperature</td>
</tr>
<tr>
<td>LengthCheck</td>
<td>False</td>
<td># Calculate average particle distance</td>
</tr>
<tr>
<td>ShowGraphs</td>
<td>False</td>
<td># Show graphs during run</td>
</tr>
<tr>
<td>SaveGraphs</td>
<td>False</td>
<td># Save graphs</td>
</tr>
<tr>
<td>UseFile</td>
<td>False</td>
<td># Post process from specific file</td>
</tr>
</tbody>
</table>

# Run Style Changes

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>LogDirectory</td>
<td>./</td>
<td># Log save directory</td>
</tr>
<tr>
<td>Parallel</td>
<td>True</td>
<td># Parallel Computation</td>
</tr>
<tr>
<td>SaveChunk</td>
<td>10000.0</td>
<td># Save to file every # iterations</td>
</tr>
<tr>
<td>SaveFiletype</td>
<td>hdf5</td>
<td># Save filetype</td>
</tr>
<tr>
<td>Scfiter</td>
<td>20</td>
<td># Self consistent loops before warning</td>
</tr>
<tr>
<td>Walltime</td>
<td>1e7</td>
<td># Run time [s]</td>
</tr>
<tr>
<td>Verbosity</td>
<td>2</td>
<td># Verbosity level</td>
</tr>
</tbody>
</table>

# Neel Relaxation Properties

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>NeelRelaxations</td>
<td>False</td>
<td># Enable Neel relaxations</td>
</tr>
<tr>
<td>NeelAnisotropicFactor</td>
<td>2.25e-08</td>
<td># Set anisotropic factor [erg*cm3]</td>
</tr>
<tr>
<td>NeelTau0</td>
<td>1.7</td>
<td># Zero value for Tau_n [1.e-12 s]</td>
</tr>
<tr>
<td>NeelTemp0</td>
<td>262.0</td>
<td># Neel zero temperature [K]</td>
</tr>
</tbody>
</table>
Appendix B

55 LSMO35 MNP Animation

An animation of the simulation seen in Fig. 5.2 is viewable in the accompanying ‘Appendix_B.mp4’ file.
Appendix C

MNP simulation frames

Figure C.1: Frames of the 5 LSMO35 MNP trajectory simulated in Fig. 5.5. The box is the periodic boundary of the system a) is at the beginning of the simulation ($t = 0$ ps), b) is a frame during the simulation ($t = 3.743 \times 10^9$ ps) and c) a frame at the end of the simulation ($t = 7.965 \times 10^9$ ps)

Figure C.2: Frames of the 10 LSMO35 MNP trajectory simulated in Fig. 5.7. The box is the periodic boundary of the system a) is at the beginning of the simulation ($t = 0$ ps), b) is a frame during the simulation ($t = 3.941 \times 10^9$ ps) and c) a frame at the end of the simulation ($t = 7.973 \times 10^9$ ps)
Figure C.3: Frames of the Twenty LSMO35 MNP trajectory simulated in Fig. 5.9. The box is the periodic boundary of the system a) is at the beginning of the simulation ($t = 0$ ps), b) is a frame during the simulation ($t = 3.833 \times 10^9$ ps) and c) a frame at the end of the simulation ($t = 7.985 \times 10^9$ ps).

Figure C.4: Frames of the 5 LSMO35 MNP trajectory simulated in Fig. 5.11. The box is the periodic boundary of the system a) is at the beginning of the simulation ($t = 0$ ps), b) is a frame during the simulation ($t = 4.217 \times 10^9$ ps) and c) a frame at the end of the simulation ($t = 7.899 \times 10^9$ ps).

Figure C.5: Frames of the 10 LSMO35 MNP trajectory simulated in Fig. 5.13. The box is the periodic boundary of the system a) is at the beginning of the simulation ($t = 0$ ps), b) is a frame during the simulation ($t = 4.140 \times 10^9$ ps) and c) a frame at the end of the simulation ($t = 7.967 \times 10^9$ ps).
Figure C.6: Frames of the 5 LSMO40 MNP trajectory simulated in Fig. 5.15. The box is the periodic boundary of the system a) is at the beginning of the simulation \((t = 0\, \text{ps})\), b) is a frame during the simulation \((t = 4.110 \times 10^9\, \text{ps})\) and c) a frame at the end of the simulation \((t = 7.947 \times 10^9\, \text{ps})\)

Figure C.7: Frames of the 10 LSMO40 MNP trajectory simulated in Fig. 5.16. The box is the periodic boundary of the system a) is at the beginning of the simulation \((t = 0\, \text{ps})\), b) is a frame during the simulation \((t = 3.974 \times 10^9\, \text{ps})\) and c) a frame at the end of the simulation \((t = 7.986 \times 10^9\, \text{ps})\)
References


[42] D.H. Manh, P.T. Phong, P.H. Nam, D.K. Tung, N.X. Phuc, and In-Ja Lee. “Structural and magnetic study of La$_{0.7}$Sr$_{0.3}$MnO$_3$ nanoparticles and AC magnetic heating characteristics for hyperthermia applications”. In: *Physica B: Condensed Matter* 444 (July 2014), pp. 94–102. DOI: 10.1016/j.physb.2014.03.025.


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