

Imperial College London
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**The effect of size, shape and oxidation on the
magnetic properties of nanoparticles**

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Submitted for the degree of Doctor of Philosophy at Imperial College London

September 2019

Declaration of originality

I confirm that the work presented in this thesis is my own. Where information has been derived from other sources, I confirm that this has been cited accordingly.

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Acknowledgements

I would first like to thank my supervisor Adrian Muxworthy for his support and help over the course of my PhD, in particular allowing me the freedom to pursue areas of research which I found appealing.

The rest of the Natural Magnetism Group at Imperial, and those who have passed through it, have helped to greatly broaden my understanding of rock magnetism (with its many applications) and provided friendly help and advice whenever needed. These include Sope Badejo, Miguel Valdez-Grijalva, Aike Supakulapos, Jay Shah, Tom Berndt, Susie Maidment, Maryam Abdulkarim, Joe Perkins, Tom North, Jude Osamor and Josh Einsle.

I was fortunate to join the Centre for Doctoral Training in Theory and Simulation of Materials at the beginning of my PhD, and I would like to thank the TSM and those within it for the many opportunities that it has offered over the past four years. A particular mention must go to the whole of Cohort 7 and Andrew Horsfield for discussions covering materials science and much more besides at our monthly lunches.

I thank Karl Fabian and Valera Shcherbakov for their help with the development of the mean-field model in providing important clarification on previous results alongside useful discussion on the results of my own work. I thank Peter Blaha and the rest of the Theoretical Chemistry group at TU Wien for hosting me in Vienna, teaching me the principles of the Wien2k DFT package and for continuing helpful advice since my visit.

Abstract

Magnetic nanoparticles are widespread in the natural environment and have potentially important biomedical and technological applications. The effect of the shape, size and level of oxidation on the magnetic properties of nanoparticles is either poorly understood, or subject to a number of conflicting results. Such effects are difficult to study experimentally and lend themselves to numerical calculations. In this thesis a number of numerical techniques were used to study magnetic nanoparticles.

A numerical mean-field model was developed to help understand the effect of particle size and shape on the Curie temperature. The Curie temperature was found to scale with particle size in agreement with the finite size scaling equation, and values of the scaling exponent were in agreement with theoretical values. The effect of shape on Curie temperature was investigated for the first time. At very small particle sizes, the Curie temperature was discovered to have a strong dependence on the particle shape below a threshold size. The threshold size was found to be controlled by the crystal structure of the magnetic material.

The Wien2k density functional theory package was used to estimate nearest neighbour exchange energies in magnetite and maghemite. Estimates of exchange energies were obtained for magnetite, but irresolvable difficulties arose in maghemite due to the presence of vacancies in the maghemite structure.

Magnetite-maghemite core-shell nanoparticles were studied using a Monte Carlo model to investigate the effect of oxidation on the magnetic properties of these systems. The Curie temperature of core-shell particles was found to increase non-linearly with increasing oxidation, likely due to the dominance of the surface in reducing the number of nearest neighbours in the maghemite shell at low levels of oxidation. Simulations of hysteresis were performed and the coercivity of a core-shell nanoparticle was found to decrease with increasing oxidation, with possible implications for magnetic hyperthermia treatment.

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Chapter 1

Introduction

1.1 Introduction to this thesis

Magnetic nanoparticles are widespread in the natural environment; for example they have been proposed as the source of magnetic anomalies over oil fields (*Abubakar et al.*, 2015) and their presence in the human brain due to inhalation of anthropogenic pollution has recently been linked to Alzheimer’s disease and other neurodegenerative diseases (*Maher et al.*, 2016). Thanks to technological advances, the properties of magnetic nanoparticles have been extensively studied over the past two decades, which has led to applications in biomedical sciences (*Parkes et al.*, 2008; *Johannsen et al.*, 2010) and magnetic recording media (*Weller et al.*, 2013).

Despite the period of study, there are still fundamental questions surrounding the behaviour of magnetic nanoparticles which remain unanswered or unclear. For example, at the nanoscale the Curie temperature scales with particle size; yet experimental (*Wang et al.*, 2011a) and numerical (*Iglesias and Labarta*, 2001; *Lyberatos et al.*, 2012) studies do not always agree with the theoretical result. In addition, the effect of shape on the Curie temperature of nanoparticles is an area which has seen little investigation.

Magnetite (Fe_3O_4) is a naturally occurring mineral which is important in rock and environmental magnetism, due to its strong magnetic moment, and biomedicine, due to its biocompatibility. When exposed to oxygen at low temperatures (e.g. natural weathering processes on an exposed outcrop), a particle of magnetite undergoes partial oxidation, in which the outer surface oxidises to maghemite ($\gamma\text{-Fe}_2\text{O}_3$) (*Gallagher et al.*, 1968; *Askill*, 1970). This creates a core-shell particle, with a core of magnetite and shell of maghemite. The magnetic behaviour of this structure has seen numerical investigation on the micrometre scale (*Ge et al.*, 2014), but studies on the nanometre scale have to date been limited to experimental investigations into the composition, structure and basic magnetic properties of these particles (*Santoyo Salazar et al.*, 2011; *Frison et al.*, 2013).

Studies into the properties of magnetic nanoparticles lend themselves well to numerical approaches. Particle properties can be exactly controlled, and a detailed picture of magnetic be-

haviour can be built from the atomic level upwards. In this thesis, the properties of magnetic nanoparticles are studied using numerical methods to answer two main questions:

1. What is the effect of particle size and shape on the Curie temperature of magnetic nanoparticles?
2. What is the effect of partial oxidation (from magnetite to maghemite) on the properties of magnetite nanoparticles?

1.2 Atomistic magnetism

Macroscopic magnetism arises from the interaction of electrons inside atoms in a crystal lattice. Electrons orbiting a nucleus contribute to an atomic magnetic moment, which subsequently interacts with neighbouring moments to align into an ordered magnetic structure. Coupling between electron orbitals and the crystal structure of a material create preferred directions of alignment along certain crystallographic axes, and impart an anisotropic contribution onto the description of magnetic systems.

1.2.1 The atomic magnetic moment

The atomic magnetic moment can be understood from the Böhr model of the atom, in which Z electrons of charge e are in circular orbits about the nucleus. The magnetic moment produced by a single electron can be described in terms of the angular momentum of the electron, $\mathbf{J}$ (Coey, 2010),

$$\mathbf{M} = \frac{e}{2m} \mathbf{J}, \quad (1.1)$$

where m is the mass of the electron. The angular momentum of the electron is quantum mechanical in nature, and is composed of an orbital component and an intrinsic spin component. The orbital angular momentum is described by $\mathbf{L} = \hbar l$ and so the magnetic moment due to $\mathbf{L}$ is (Coey, 2010),

$$\mathbf{M}_L = \frac{e\hbar}{2m} l = -\mu_B l, \quad (1.2)$$

where $\hbar$ is the reduced Planck's constant ($\hbar = h/(2\pi)$), l is the magnetic quantum number and μ_B is the Böhr magneton. Similarly, the intrinsic spin of the electron has angular momentum $\mathbf{S} = \hbar s$ which gives rise to a magnetic moment of (Coey, 2010),

$$\mathbf{M}_S = -g\mu_B s, \quad (1.3)$$

where s is the spin of the electron ($\pm 1/2$), and g is the g-factor $g = 2.002 \approx 2$ (Odom et al., 2006). Filled electron shells have net zero angular momentum due to the Pauli exclusion principle, and

so only unfilled shells contribute to the magnetic moment of an atom (Figure 1.1). In elements of interest to magnetism, the spin and angular momenta of electrons generally follow the LS coupling scheme. Individual spin and orbital angular momenta add to give resultant quantum numbers (Coey, 2010),

$$L = \sum_{i=1}^Z l_i, \quad S = \sum_{i=1}^Z s_i, \quad J = S + L. \quad (1.4)$$

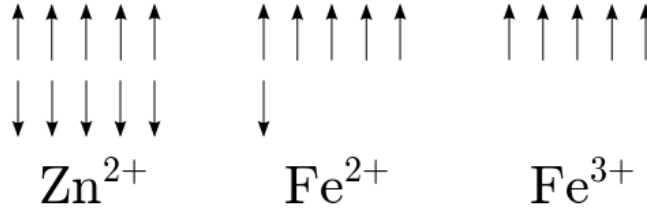


Figure 1.1: The 3d shell contains up to 10 electrons in different states. Zn^{2+} has a full 3d shell, and so no net angular momentum or magnetic moment. Fe^{2+} and Fe^{3+} both have unfilled 3d shells, and so possess a magnetic moment.

The 3d transition metals are an important class of magnetic elements containing, amongst others, Fe, Co and Ni. In these elements the 3d electron shell is the outermost shell, and when part of a crystalline structure it interacts strongly with the crystal field of neighbouring ions. This leads to a quenching of the orbital angular momentum of the 3d electrons. The spin angular momentum is unaffected by this interaction and so the magnetic moment of 3d transition elements is due only to unpaired electron spins (Figure 1.2).

1.2.2 Exchange energy

Exchange energy arises from consideration of the energy required to exchange two electrons with different spins at different positions (see Chikazumi (2010) for more detail),

$$\psi_{\uparrow}(r_1) \psi_{\downarrow}(r_2) \rightarrow \psi_{\uparrow}(r_2) \psi_{\downarrow}(r_1). \quad (1.5)$$

where $\psi_{\uparrow}(r_1)$ is the wavefunction of the spin up electron at position r_1 and $\psi_{\downarrow}(r_2)$ is the wavefunction of the spin down arrow at position r_2 . Heisenberg (1928) originally only considered the exchange of single spin half electrons; however, if each unpaired electron in an atom has the same exchange integral with each unpaired electron in the neighbouring atom, then the values of S_i and S_j in equation (1.6) may be taken as the total spin of the atom (White, 2007). The interaction of two atoms in this manner is known as direct exchange to distinguish it from superexchange, which is described below.

The exchange energy may be mathematically expressed (Fisher, 1964),

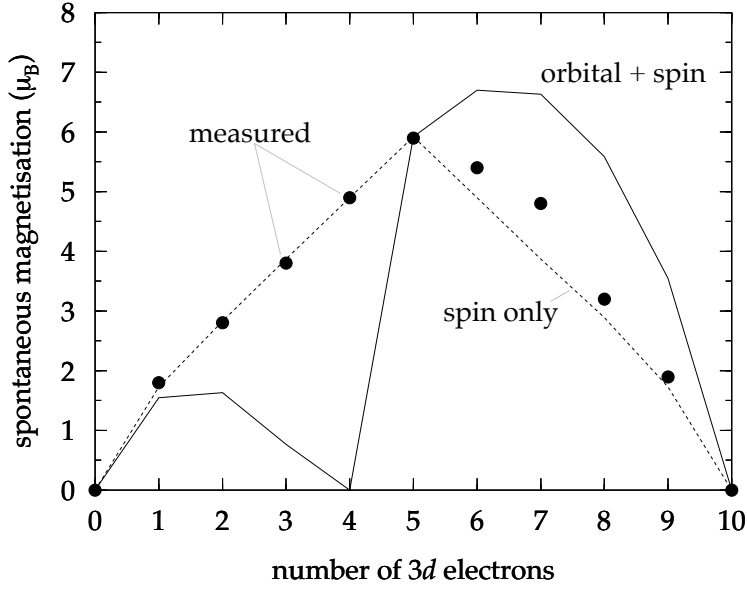


Figure 1.2: Spontaneous magnetisation of 3d transition metal elements. Theoretical curves considering orbital and spin angular momentum and spin only angular momentum are shown in comparison to experimental values. Below five 3d electrons, the measured moment is identical to a spin only contribution. For more than five 3d electrons, some orbital angular momentum is unquenched due to Russell-Saunders coupling. Image taken from Muxworthy (1998), after Jiles (1991).

$$\mathcal{H}_{ex} = -2 \sum_{\langle ij \rangle} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j, \quad (1.6)$$

where S_i is the spin of site i , J_{ij} is the exchange energy between sites i and j , and the sum over $\langle ij \rangle$ is over nearest neighbour pairs.

The value of J_{ij} may be positive or negative. When J_{ij} is positive, spins align parallel to one another in order to minimise energy, and this leads to ferromagnetic behaviour. A negative value of J_{ij} leads to an anti-parallel alignment of interacting spins. In antiferromagnetic and ferrimagnetic materials there is a negative exchange energy between two sub-lattices of atoms, with either a positive or more weakly negative interaction between atoms within the sub-lattices. This leads to the parallel alignment of spins within a sub-lattice, with each sub-lattice aligned anti-parallel.

Superexchange

Superexchange, occurs between two cations separated by an anion; for example, between the two Fe^{2+} ions in a $\text{Fe}^{2+}\text{-O}^{2-}\text{-Fe}^{2+}$ linkage. The wavefunctions of the two Fe atoms do not appreciably

overlap, and so any direct exchange between them is very weak. However, many such systems, e.g. iron oxides, exhibit magnetic properties. The theory of superexchange was proposed by *Kramers* (1934) to explain how the exchange mechanism works in such systems.

The O^{2-} ion has the electronic structure $(1s^2)(2s^2)(2p^6)$. One of the $2p$ electrons may transfer to an unpaired $3d$ orbital of an Fe^{2+} ion and must conserve its spin. Due to the constraints imposed by Hund's rules (*Chikazumi*, 2010), the transferred electron has a spin anti-parallel to the overall spin of the Fe ion. The now unpaired electron in the oxygen anion, which points anti-parallel to the transferred electron due to the Pauli exclusion principle, now enters a direct exchange with the other Fe atom. From this, it is possible to calculate an effective exchange between the two Fe ions, and this interaction behaves as in equation (1.6).

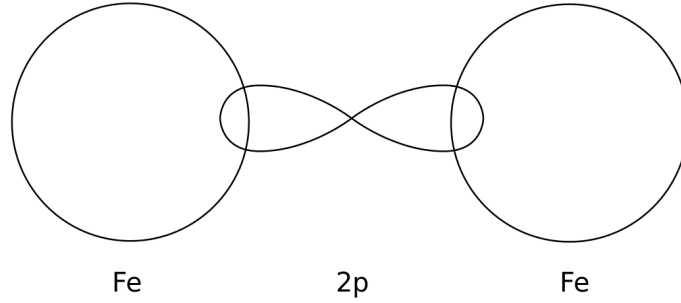


Figure 1.3: Overlap between wavefunctions of a $2s$ electron orbital and Fe^{2+} ions in a $Fe^{2+}-O^{2-}-Fe^{2+}$ linkage. Image adapted from (*Anderson*, 1963).

Due to the angular distribution of the $2p$ orbital, the maximum of wavefunction overlap (and so the strongest exchange) occurs when the angle formed between the cation-anion-cation linkage is 180° (Figure 1.3) (*Anderson*, 1950). The semi-empirical Goodenough-Kanamori rules show that there exists an angular dependence on the value of exchange energy (*Goodenough*, 1955; *Kanamori*, 1959); it is generally negative, with a maximum magnitude at 180° and shrinks in magnitude as the angle reduces. At around 90° the value of the exchange integral is typically small and positive.

1.2.3 Anisotropy energy

Magnetocrystalline anisotropy

Magnetocrystalline anisotropy (MCA) arises from spin-orbit coupling between electron orbitals and electron spins (*Getzlaff*, 2008). The orientations of the electronic orbitals are coupled to the crystal structure of a material, and this in turn leads to the preferential alignment of spins along certain crystallographic axes. Whilst this means that expressions for the MCA energy can in theory be derived from first principles, in practice phenomenological expressions are used instead.

Uniaxial anisotropy is the simplest form of MCA and occurs in materials exhibiting a hexagonal crystal structure. There are two magnetic easy directions corresponding to a minimum of MCA energy, which point up and down the crystallographic c -axis. The total uniaxial anisotropy energy is given by (*Chikazumi*, 2010),

$$E_a = K_{u1} \sin^2 \theta + K_{u2} \sin^4 \theta + K_{u3} \sin^6 \theta + \dots, \quad (1.7)$$

where θ is the angle between the c -axis and the magnetisation, and K_{u1} , K_{u2} , K_{u3} are material and temperature dependent anisotropy constants given in units of Jm^{-3} .

In cubic crystals, the anisotropy is described in terms of the direction cosines formed between the magnetisation vector and the edges of the cubic structure (the $[100]$, $[010]$, and $[001]$ directions). The expression for cubic anisotropy is (*van Vleck*, 1937),

$$E_a = K_1 (\alpha_1^2 \alpha_2^2 + \alpha_2^2 \alpha_3^2 + \alpha_3^2 \alpha_1^2) + K_2 \alpha_1^2 \alpha_2^2 \alpha_3^2 + \dots \quad (1.8)$$

where K_1 and K_2 are again material and temperature dependent constants, and α_1 , α_2 and α_3 are the direction cosines. In many cases, K_1 is much larger than K_2 and so can be considered the dominant term. Owing to the high symmetry of the cubic lattice, there are three easy axes along the $[100]$, $[010]$ and $[001]$ directions when $K_1 > 0$ and four easy axes along $[111]$, $[\bar{1}11]$, $[1\bar{1}1]$ and $[11\bar{1}]$ directions when $K_1 < 0$.

When considering MCA on an atomistic level the anisotropy energy can be given in terms of the spin of each magnetic site. The Hamiltonian for cubic anisotropy can therefore be described by (*Mazo-Zuluaga et al.*, 2009),

$$\mathcal{H}_a = -K_V \sum_i (S_{i,x}^2 S_{i,y}^2 + S_{i,y}^2 S_{i,z}^2 + S_{i,x}^2 S_{i,z}^2), \quad (1.9)$$

where $K_V = K_1$ is given in energy per spin and i is a sum over all sites in the system.

Surface anisotropy

Néel (1954) proposed that the broken symmetry of the crystal lattice at the surface of a magnetic material results in a different form of anisotropy, which he called surface anisotropy. An increase in anisotropy energy (in Jm^{-3}) as particle size decreases has been seen in nanoscale α -Fe, $\text{Fe}_{1-x}\text{C}_x$, magnetite, and hematite particles, an effect which is attributed to surface anisotropy (*Mørup and Topsøe*, 1976; *Christensen et al.*, 1985; *Bødker et al.*, 1994). Experimental studies on the values of the surface anisotropy constant suggest values of $1 - 500 \times 10^{-3} \text{ Jm}^{-2}$ (*Berger et al.*, 2008). When considered in terms of Joules per spin, this is approximately an order of magnitude larger than typical values for the magnetocrystalline anisotropy constant.

The phenomenological Hamiltonian for *Néel's* surface anisotropy model is (*Jamet et al.*, 2004),

$$\mathcal{H} = -K_S \sum_i (\mathbf{S}_i \cdot \mathbf{e}_{ij})^2, \quad (1.10)$$

where K_S is the surface anisotropy constant, the sum over i is over all surface spins and $\mathbf{e}_{ij}$ is the normalised resultant direction vector formed from the sum over all nearest neighbour directions. It is approximately normal to the surface of the particle and is expressed by,

$$\mathbf{e}_{ij} = \sum_{j=1}^{z_i} \frac{\mathbf{r}_i - \mathbf{r}_j}{r_{ij}}, \quad (1.11)$$

where $\mathbf{r}_i$ is the location vector of spin i , and r_{ij} is the distance between spin i and spin j .

Monte-Carlo studies focussing on the ratio $\frac{K_S}{K_V}$ in simple cubic and magnetite nanoparticles have suggested the emergence of new types of spin states for different values of $\frac{K_S}{K_V}$ (*Berger et al.*, 2008; *Mazo-Zuluaga et al.*, 2009). An alternative approach to modelling the surface anisotropy was taken by *Bødker et al.* (1994) where they instead considered an effective anisotropy constant, replacing K_V with,

$$K_{eff} = K_V + K_S \frac{S}{V}, \quad (1.12)$$

where V is the volume of the particle and S the surface area. For a spherical nanoparticle, this gives,

$$K_{eff} = K_V + \frac{6}{d} K_S, \quad (1.13)$$

where d is the diameter of the particle. Agreement to this model has been found for some systems, such as α -Fe nanoparticles (*Bødker et al.*, 1994). However, this model does not appear to be universal, and has failed to describe systems of hematite and maghemite (*Mørup and Ostenfeld*, 2001).

1.2.4 External Field

The presence of an external field causes spins to preferentially align in the direction of that field. An external field couples to each atomic spin in the system, and can be mathematically expressed by (*Woodgate*, 1983),

$$\mathcal{H}_H = -g\mu_B \mathbf{H} \cdot \sum_i \mathbf{S}_i, \quad (1.14)$$

where $\mathbf{H}$ is the external magnetic field.

1.3 Magnetic nanoparticles

1.3.1 Single domain particles

Magnetic materials typically split up into magnetic domains, with each domain having a different magnetisation direction in a process driven by magnetostatic energy. However below a critical diameter, magnetic particles do not split into multiple domains, and possess only a single domain (*Frenkel and Doefman*, 1930). The critical diameter, d_c , for a ferromagnetic sphere is approximately (*O’Handley*, 2000),

$$d_c = \frac{18\sqrt{A_{ex}K}}{\mu_0 M_S^2} \quad (1.15)$$

where A_{ex} is the exchange stiffness, K is the uniaxial anisotropy constant, μ_0 is the permeability of free space and M_S is the saturation magnetisation. The critical diameter therefore depends on the material, but is typically in the range 5 – 1000 nm. For Fe, d_c is 25 nm and for magnetite it is about 60 nm (*O’Handley*, 2000; *Muxworthy and Williams*, 2015). Single domain particles are uniformly magnetised to their spontaneous magnetisation, and due to the lack of domain walls, are magnetically harder than multi-domain systems.

1.3.2 Superparamagnetism

In very small particles, the direction of magnetisation may spontaneously reverse due to thermal agitation (*Néel*, 1949; *Brown*, 1963) and so exhibit superparamagnetic behaviour. A magnetised particle must overcome an energy barrier due to anisotropy in order to switch the direction of its magnetisation, and this energy barrier is proportional to the volume of particle. The probability of a reversal of the magnetisation is negligible for large particles, but significant for very small ones. Over the course of an experimental measurement, an assemblage of very small particles will undergo a large number of these reversals in magnetisation direction, and the overall magnetisation may appear close to that of a paramagnetic system.

The first theoretical treatment of superparamagnetic behaviour was undertaken by *Néel* (1949) considering uniaxial ferromagnetic particles. He assumed that the magnetic moments of each particle are always in one of the two energy minima corresponding to opposing magnetisation directions, and from this derived the equation for the average time between reversals,

$$\tau = \tau_0 \exp\left(\frac{KV}{k_B T}\right), \quad (1.16)$$

where τ_0 is typically of the order $10^{-10} - 10^{-9}$ s, K is the uniaxial anisotropy constant and V is the volume of the particle. Later work by *Brown* (1963) using the Langevin equation improved upon this and found that τ_0 was in fact weakly temperature dependent,

$$\tau_0 = \frac{1 + (\eta\gamma M_S)^2}{\eta\gamma^2} \frac{\sqrt{\pi}}{4K} \left(\frac{k_B T}{KV} \right)^{1/2}, \quad (1.17)$$

where η is a dissipation constant, γ is the gyromagnetic ratio and M_S is the saturation magnetisation. The above equations are a good approximation when $\frac{KV}{k_B T} > 1$, but when $\frac{KV}{k_B T} < 1$ then the relaxation has no dependency on anisotropy and the relaxation time is instead given by (Aharoni, 1973),

$$\tau = \frac{M_S V}{\gamma k_B T}. \quad (1.18)$$

1.3.3 The magnetic structure of nanoparticles

Atoms on the surface of a magnetic material experience a different environment to atoms located in the bulk. There is a reduction in the number of nearest neighbours, and a material may undergo structural changes to the lattice leading to vacancies or changes to bond length (Bliem *et al.*, 2014). As a result of this, surface spins behave differently to spins in the bulk leading to a change in magnetic behaviour on the surface. In the case of nanoparticles, a substantial fraction of the total number of atoms in the particle lie on the surface, and so surface effects play an important role in the overall magnetic behaviour of nanoparticles.

Increased magnetic moment in small clusters

Studies of small clusters, 20-700 atoms in size, of 3d metals (Fe, Ni and Co) have revealed an enhanced average magnetic moment in many of these systems (Bucher *et al.*, 1991; Billas *et al.*, 1994). The average moments were found to transition from a value close to that of a free Fe/Ni/Co atom to a moment close to the value found in the corresponding elemental ferromagnet as the cluster size increased to around 400 atoms. Electronic structure calculations of cobalt clusters of 4-19 atoms suggest that the average moment of these clusters is strongly linked the symmetry of the cluster. The corresponding degeneracy of the 3d electrons in the cobalt atoms leads to different levels of bonding with neighbour atoms, and thus different values of magnetic moment (Li and Gu, 1993).

Reduction in surface magnetisation

Behaviour at the surface of a magnetic particle is difficult to determine experimentally, as the spatial origin of a signal is hard to isolate. With the exception of particularly small particles numbering a handful of atoms, experimental data from any particle will be a mixture of the properties of atoms in the interior and surface.

A pure signal from the surface of iron oxide nanoparticles was achieved by Shinjo *et al.* (1983) using ^{57}Fe Mössbauer spectroscopy. By preparing a core of hematite ($\alpha\text{-Fe}_2\text{O}_3$) using pure ^{56}Fe ,

with a thin outer layer of ^{57}Fe , they were able to observe the signal from the surface. They found a clear reduction in the surface magnetisation with respect to the bulk value for all temperatures (Figure 1.4). Simple theoretical calculations which applied a reduced exchange interaction to the surface of 60% of the bulk value reproduced the results with good accuracy.

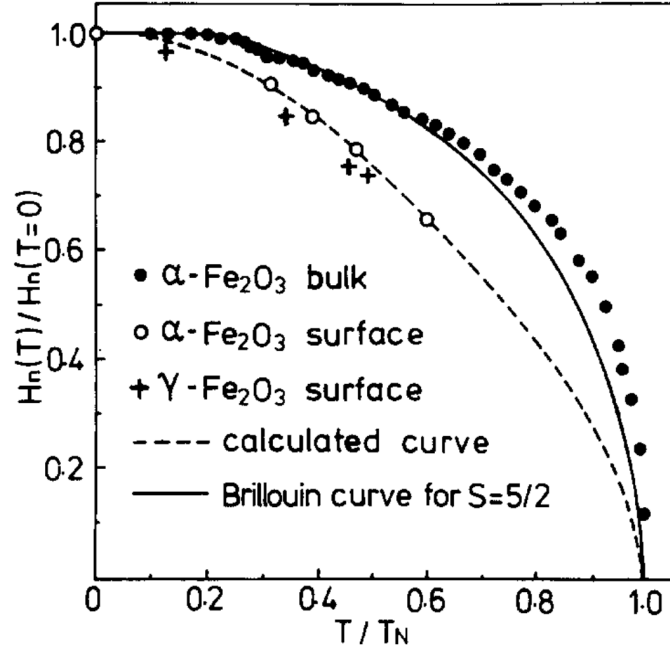


Figure 1.4: Normalised hyperfine field for bulk $\alpha\text{-Fe}_2\text{O}_3$ (hematite) and the surface of both $\alpha\text{-Fe}_2\text{O}_3$ and $\gamma\text{-Fe}_2\text{O}_3$ (maghemite) nanoparticles. The solid line is the Brillouin curve for bulk exchange, and the dashed line is the Brillouin curve for the surface atoms, assuming a reduced surface exchange of 0.6 of the bulk value. The temperature dependence of the hyperfine field has been assumed the same as the magnetisation. From Shinjo *et al.* (1983)

Owing to the difficulty in distinguishing signals from the surface, investigations of this type lend themselves to computational studies, where the magnetic behaviour of the surface can be easily studied in isolation. Shcherbakov *et al.* (2012) investigated the magnetisation of bcc cubic nanoparticles using a numerical mean field model. They found a reduction in surface magnetisation across all temperatures (Figure 1.5). At low temperatures, only surface atoms showed any significant reduction in magnetisation. As the temperature increased towards T_C , the region of reduced magnetisation spread inwards towards the core of the particle.

Surface spin canting

The spins at the surface of a nanoparticle exhibit other types of unusual behaviour. Magnetic spin canting is a phenomena in which the spins of a magnetic material are not exactly aligned, but instead are orientated with a non-zero angle between their directions.

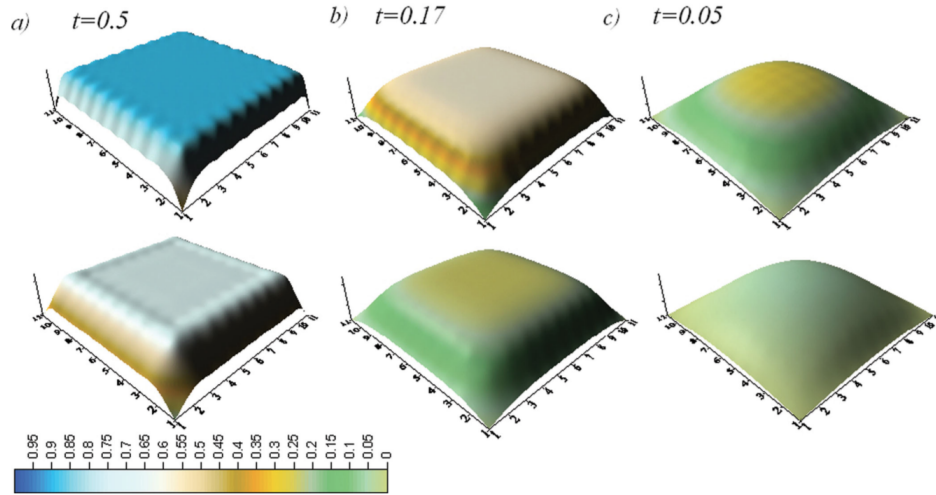


Figure 1.5: Magnetisation of layers in the (001) direction of a bcc cubic nanoparticle with 21 layers. The top row shows magnetisation of the central layer, and the bottom row shows the magnetisation across the surface layer. Graphs (a)-(c) show these magnetisation profiles for a range of reduced temperatures $t = \frac{T_C - T}{T_C}$. From Shcherbakov *et al.* (2012).

When an external field is applied to a pure ferrimagnetic material, the magnetisation is expected to align with that applied field. When this is studied with Mössbauer spectroscopy, the relative area of the six spectral lines are given by $3 : x : 1 : 1 : x : 3$ where (Morrish and Haneda, 1983),

$$x = \frac{4 \sin^2 \theta}{(1 + \cos^2 \theta)}, \quad (1.19)$$

with θ the angle between the hyperfine field and the gamma ray direction. Therefore, if the external field is applied parallel to the gamma ray direction, the hyperfine field should also align, so for $\theta = 0$, the second and fifth lines of the spectra will vanish.

Experimental work conducted by Coey (1971) showed that for γ -Fe₂O₃ crystals of diameter ~ 6 nm, the second and fifth lines of such Mössbauer spectra did not vanish, even in an applied field of 50 kOe (Figure 1.6). A core of aligned spins, with a surface layer of non-random yet non-aligned spins was interpreted as the likely structure from analysis of the measured magnetic moment, yet possible spin canting in the interior could not be disproved. Further work using Mössbauer spectroscopy by Morrish and Haneda (1983) seemed to confirm that spin canting was almost exclusively a surface effect and additionally suggested, from a broadening of the second and fifth line-widths, that the distribution of canting angles increased with temperature. More recent work has shown that spin canting is not confined to the surface, with the degree of canting dependent on the overall structural disorder of the particle (Morales *et al.*, 1997; Serna *et al.*, 2001).

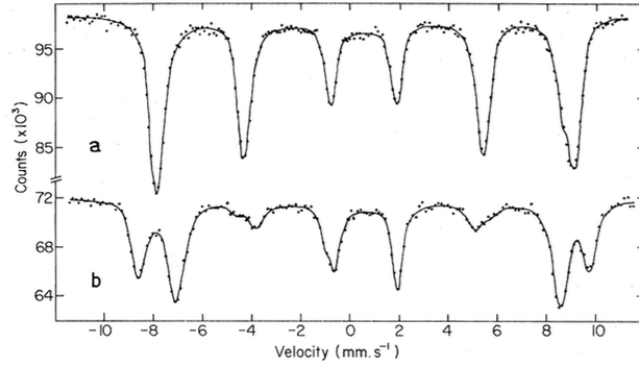


Figure 1.6: Mössbauer spectra of 6nm γ -Fe₂O₃ crystals at 5 K, a) without and b) with an external field of 50 kOe applied parallel to the gamma ray direction. From Coey (1971).

1.3.4 Phase transitions

In bulk magnetic systems, the spin correlation length diverges at the Curie temperature, T_C , but in nanoscale systems the growth of the correlation length is limited by the smallest dimension of the system such that it causes a reduction in T_C . This obeys a finite-size scaling relationship (Fisher and Ferdinand, 1967),

$$\frac{T_C(\infty) - T_C(d)}{T_C(\infty)} = \left(\frac{d_0}{d}\right)^{\frac{1}{\nu}} \quad (1.20)$$

where $T_C(\infty)$ is the bulk Curie temperature, d_0 is a characteristic length scale of the system, ν is the correlation length scaling exponent and d is the smallest length scale of the system. An early study of nanoscale MnFe₂O₄ reported a surprise increase in Curie temperature with reducing size which fit a finite-size scaling law (Tang *et al.*, 1991). This effect was shown to be due to the sensitivity of T_C on the distribution of Mn across the A and B sites of the spinel structure, which itself changes with particle size (Brabers, 1992; van der Zaag *et al.*, 1992). Recent developments in preparation techniques have lead to several new experimental investigations of finite-size scaling in magnetic nanoparticles (e.g. Wang *et al.*, 2011b). However, the results have been varied in contrast with the good agreement between theory and experiment found in studies of thin films (Huang *et al.*, 1993; Ambrose and Chien, 1996). Studies of hematite and magnetite nanoparticles have found values for ν in the range of 0.6 – 0.8 (Wang *et al.*, 2011b; Li *et al.*, 2014), close to the expected value of 0.7043 (Chen *et al.*, 1993) for the 3-D Heisenberg model. A value of $\nu = 1.06$ was determined from work conducted on Ni nanoparticles (Wang *et al.*, 2011a), with line dislocations near the surface of the nanoparticles suggested as the cause of this discrepancy.

Monte Carlo modelling of nano-scale systems has failed to clarify the situation, with values of ν derived from finite-size scaling also failing to agree with the accepted value of the correlation length scaling exponent. An Ising Monte Carlo simulation of maghemite nanoparticles suggested a value of $\nu = 0.49$ from finite sized scaling (Iglesias and Labarta, 2001), in clear disagreement

with the 3-D Ising value of 0.6417 calculated from consideration of thermodynamic derivatives (*Ferrenberg and Landau*, 1991). Simulations of L1₀-FePt using a classical-spin Heisenberg model determined a value of $\nu = 1.06$ (*Lyberatos et al.*, 2012), again disagreeing with the generally accepted value. Long-range ordering was suggested as a possible source of this disagreement.

Shcherbakov et al. (2012) used Ginzberg-Landau theory to obtain analytic expressions for the Curie temperatures of magnetic thin-films and cubic nanoparticles. For thin-films, they obtained a modified scaling law,

$$t_0 = \frac{T_C(\infty) - T_C(N_t)}{T_C(\infty)} \approx \left(\frac{\pi}{\sqrt{2}(N_t + 2)} \right)^{\frac{1}{\nu}}, \quad (1.21)$$

and cubic nanoparticles, a similar expression,

$$t_0 \approx \left(\frac{\sqrt{3}\pi}{\sqrt{2}(N_d + 2)} \right)^{\frac{1}{\nu}}, \quad (1.22)$$

where N_t is the number of layers of the thin-film and N_d is the width of the cubic particle (in number of layers). Using the value of ν from the Heisenberg model ($\lambda = 0.704$), the theoretical value of the Curie temperature was compared to the experimental data of *Li and Baberschke* (1992) for Ni thin films. Whilst the shape of the relationship between N_t and t_0 was well reproduced by the analytical expression (equation 1.21), the theoretical predictions of t_0 were consistently 10 – 20% lower than the experimental values.

Other phase transitions

Other magnetic phase transitions also show a change in critical temperature with reduced particle size. In hematite, the Morin transition occurs at the Morin temperature, T_M , and is a transition in the direction of the magnetisation. Below the Morin temperature, the sublattice magnetisations are aligned parallel to the hexagonal [001] direction (*Morin*, 1950). Above T_M , the direction changes to become perpendicular to its previous orientation, with a small angle between sublattice magnetisation directions. The Morin temperature in hematite nanoparticles (of size 10-18 nm) was studied using Mössbauer spectra and found to be reduced for small particles (*Kündig et al.*, 1966). The increase in anisotropy constant with reducing size was proposed as part of the mechanism for the reducing Morin transition (*Klausen et al.*, 2004). The Verwey transition (*Verwey*, 1939) in magnetite (see section 2.5.2 for details) has also been observed to reduce with decreasing particle size (*Mørup and Topsøe*, 1983; *Poddar et al.*, 2002).

1.3.5 Exchange bias

Exchange bias was discovered by *Meiklejohn and Bean* (1956) whilst investigating the properties of core-shell Cobalt particles ~ 200 Å in size. These particles consisted of a ferromagnetic cobalt core with a shell of antiferromagnetic cobalt oxide (CoO). When the sample was cooled in an

applied field through the Néel temperature of CoO, the subsequent low-temperature hysteresis loops were shifted horizontally. This shift is explained by exchange bias.

Figure 1.7 shows a schematic illustration of how the effect works. It is described here in terms of a cobalt core-shell particle, but is equally applicable to a thin film system. The system begins at a temperature greater than the Néel temperature of the anti-ferromagnetic shell. An external field is applied and the spins of the ferromagnetic core align in the direction of the field (1). When the sample is field cooled below the Néel temperature, the antiferromagnetic cobalt oxide layer aligns such as to minimise the energy along the interface (2). When the applied field is varied in the low-temperature regime, the cobalt oxide interacts with the cobalt core through the exchange interaction (3-5). The arising exchange field along the interface acts as an effective applied field. As a result, the strength of external field required to reverse the magnetisation direction changes and causes a shift in the hysteresis loop.

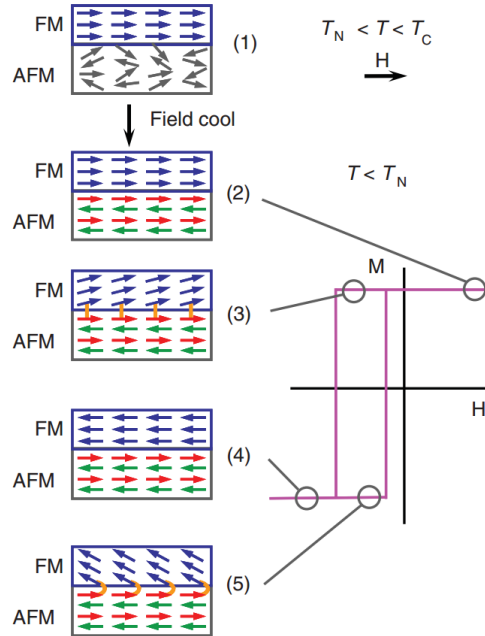


Figure 1.7: Schematic diagram of exchange bias effect of a ferromagnetic-antiferromagnetic bilayer at different stages of a hysteresis loop. From Mørup *et al.* (2011) and adapted from Nogués and Schuller (1999).

From the description above, exchange bias should be constrained to thin film or fine particle systems containing an antiferromagnetic-ferro/ferri-magnetic interface. Despite this, exchange bias has been found in core-shell nanoparticle systems with a core of α -Fe and a shell of maghemite/magnetite. Analysis of the Mössbauer spectra of these systems has revealed spin canting in the iron oxide layer which was interpreted as inducing the observed exchange bias (Zheng *et al.*, 2004).

Mechanically alloyed mixtures of ferromagnetic Co and antiferromagnetic NiO or FeS powders

have shown an increased coercivity compared with Co nanoparticles. This has been directly linked to the exchange bias effect and has led to suggestions that such techniques could be used to create new types of permanent magnets (*Sort et al.*, 1999).

1.3.6 Applications and impacts of magnetic nanoparticles

Magnetic nanoparticles in the environment

Magnetic nanoparticles are widespread in nature and are found in rocks, soils and airborne matter (*Prévoit et al.*, 1981; *van Velzen and Dekkers*, 1999; *Maher et al.*, 2016). Two examples of the possible uses and implications of magnetic nanoparticles in the environment are given here.

In the 1970s, aerial surveys identified magnetic anomalies over oil fields (*Donovan et al.*, 1979). Recent work has demonstrated that magnetic nanoparticles of diameter less than 10 nm are formed in oil generating conditions inside source rock (*Abubakar et al.*, 2015). The particles are able to pass through the pore-throat of many sandstones and so in principle migrate with the oil throughout the reservoir. This suggests that at least part of the magnetic signal detected may be due to nanoparticles created during the oil formation process, and opens up the possibility of using these particles as a tool for understanding oil and gas reservoirs.

Magnetite nanoparticles formed from combustion or frictional heating are found in airborne particulate matter and identical particles have also been identified in the human brain (*Maher et al.*, 2016). Airborne magnetite nanoparticles of diameter less than 200 nm are able to enter the brain directly through the olfactory nerve and by crossing the damaged olfactory unit. Magnetite is known to be toxic to brain tissue, and has been linked to Alzheimer's disease and other neurodegenerative conditions.

Biomedicine

There are a number of medical applications of magnetic nanoparticles. Iron oxides are frequently used due to their biocompatibility. Typically, nanoparticles used in biomedical applications are treated with a surfactant in order to make them hydrophilic (*Mornet et al.*, 2004).

Magnetic hyperthermia can be used as a treatment for cancer (*Mornet et al.*, 2004; *Pankhurst et al.*, 2009). Tumours are heated by applying an alternating magnetic field to a ferromagnetic material which is located in the tumour. Injecting nanoparticles into the treatment site offers an attractive advantage over inserting larger rods of material into a particular location, as this reduces unnecessary tissue damage.

Magnetic nanoparticles are also used as contrast agents in magnetic resonance imaging (MRI) scans. MRI monitors the decay of the magnetisation of nuclei after they have been excited by radio-frequency magnetic pulses (*Mornet et al.*, 2004). The inclusion of magnetic nanoparticles increases the contrast in areas where they are present and has become important in the diagnosis of liver cancer. Healthy Kupffer cells in the liver absorb magnetic nanoparticles, but cancerous

tissue does not (*Pankhurst et al.*, 2003). The increased contrast seen in the MRI scan then allows a diagnosis to be made.

Magnetic drug delivery is another technique being investigated (*Pankhurst et al.*, 2009). Currently, drugs are injected or absorbed into the body and affect tissue as a whole. This either causes damage to otherwise healthy cells, such as in chemotherapy, or results in a weaker concentration of active ingredient reaching parts of the body requiring treatment. If drugs are delivered inside or attached to magnetic nanostructures, external magnetic fields can be used to concentrate drugs into the optimal location, and so increase their effectiveness.

Magnetic recording

The magnetic storage of information on hard drives and other magnetic media is now ubiquitous (*Wood*, 2009). Information is written to the media using a write head, which generates a localised magnetic field. During writing, the magnetisation directions of the individual grains are aligned in two antiparallel directions, which correspond to the binary ones and zeros of data bits.

Since the first magnetic hard disk was introduced in 1956, areal bit density has grown exponentially, driven by a huge decrease in the bit size (*Wood*, 2009). However, eventually bit sizes will become so small that information is lost to superparamagnetic relaxation. Commercial disks in the present day currently take advantage of perpendicular recording. By making the bits thicker, this technique allows a smaller bit area to be realised, whilst keeping a large enough volume to avoid superparamagnetic relaxation. Current research on further improvements has focussed on using Co-Cr-Pt alloys which have a high magnetic anisotropy such that a sufficiently large energy barrier between the easy-axis is present in ever smaller particles (*Weller et al.*, 2013). A higher anisotropy also increases the coercivity of the grains, which in turn require a higher applied field to change the orientation of the magnetisation during writing- a further engineering challenge.

Two avenues of research are being pursued for the next generations of magnetic recording. Current technology uses a medium of randomly placed particles on which to write information. Replacing this with a precisely determined pattern of single-domain islands, each representing a single bit, is likely to be the next step in improving bit densities (*Moser et al.*, 2002; *Terris and Thomson*, 2005). Heat-assisted magnetic recording is also a focus of study and uses local heating of the recording medium by a laser to heat the recording grain above T_C and so temporarily reduce the coercivity during writing (*Weller et al.*, 2013).

1.4 Magnetic minerals

In this section the properties of the natural magnetic minerals magnetite and maghemite are discussed, as they are both studied as part of this thesis. It should be noted that other important naturally occurring magnetic minerals do exist, e.g., greigite and titanomagnetite, but are beyond

the scope of this thesis. The properties of magnetite-maghemite particles are also discussed.

1.4.1 Magnetite

Magnetite (Fe_3O_4) is a ferrimagnetic iron oxide. It is naturally occurring and strongly magnetic, and is often considered the most important magnetic mineral on Earth (*Dunlop and Özdemir, 1997*). Its properties have therefore been extensively studied.

Magnetite undergoes two solid state phase transitions; the typical magnetic ordering transition, with a Curie temperature of 850K (*Dunlop and Özdemir, 1997*) and, as previously mentioned, an insulator-semiconductor transition known as the Verwey transition at 125K (*Yoshida and Iida, 1977*).

Structure

Magnetite forms in the spinel crystal structure (*Verwey and Heilmann, 1947; Shull et al., 1951*). The unit cell contains 56 atoms with a lattice constant of $a = 8.39\text{\AA}$ (*Chikazumi, 2010*). 36 oxygen ions (O^{2-}) are arranged in a face-centred cubic lattice, with the iron cations occupying interstitial sites which correspond to 8a (tetrahedral) and 16d (octahedral) Wyckoff positions in the $Fd3m$ space group (*Grau-Crespo et al., 2010*). Eight tetrahedral (A) sites are occupied by Fe^{3+} ions and sixteen octahedral (B) sites are occupied by an equal number of randomly distributed Fe^{2+} and Fe^{3+} ions (Figure 1.8). Magnetite is considered to have an inverse spinel structure due to the distribution of the Fe^{3+} ions across both A and B sites. The magnetic moments of the A and B sites are aligned anti-parallel to form the ferrimagnetic sublattices.

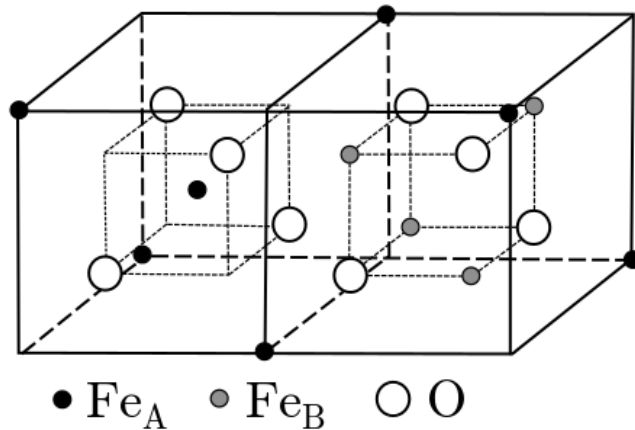


Figure 1.8: Structure of magnetite showing two octants of the unit cell. The octants are arranged in a chess board pattern to form the unit cell.

The electronic configuration of iron is $[\text{Ar}]3d^64s^2$. Iron is a transition metal, and so the 4s electrons are preferentially lost during ionisation. Consideration of Hund's rules for the unfilled 3d

shell assigns magnetic moments of $4\mu_B$ to Fe^{2+} and $5\mu_B$ to Fe^{3+} ions (*Zhang and Satpathy, 1991*), leading to an expected magnetic moment of $4\mu_B$ per formula weight. This is in good agreement with the experimental value of $4.1\mu_B$ (*Weiss and Forrer, 1929*).

Exchange energies

Superexchange interactions in magnetite between the Fe ions occur through the intervening oxygen atoms (*Chikazumi, 2010*). A-O-B atom pairs have an angle closer to 180° than A-O-A pairs. It would therefore be expected that the J_{AB} interaction is a stronger negative interaction than J_{AA} . The B-O-B pair has an angle close to 90° (see Figure 1.8), and so the value of J_{BB} is likely to be weak and positive. A site ions have $z_{AA} = 4$ nearest neighbour A-O-A interactions and $z_{AB} = 12$ nearest neighbour A-O-B interactions. B sites have $z_{BA} = z_{BB} = 6$ nearest neighbour A-O-B and B-O-B interactions. Details of the locations of nearest neighbours for each site are given in Table 1.1.

Estimates for the values of nearest neighbour exchange energy were calculated from neutron scattering (*Brockhouse and Watanabe, 1963; Bourdonnay et al., 1971*), by consideration of a range of experimental results (*Möglestue, 1968*) and by magnetic susceptibility (*Néel, 1948*). *Ab initio* density functional theory calculations were carried out by *Uhl and Siberchicot (1995)* to estimate exchange interactions using spin spiral configurations. The results of these studies are summarised in Table 1.2.

In all experimental cases, J_{AB} is the dominant negative interaction, and J_{BB} is weak and generally positive. J_{AA} , where measured, is typically a weaker negative interaction. The general behaviour of the measured exchange interactions is therefore in good agreement with the behaviour expected from superexchange theory. *Brockhouse and Watanabe (1963)* were able to make a good estimate of the J_{AB} interaction and felt that their value had an accuracy of better than 10%. Their results also suggested a weak ferromagnetic J_{BB} interaction was likely but were unable to investigate the J_{AA} interaction. The results obtained by *Bourdonnay et al. (1971)* and *Möglestue (1968)* are in good agreement, and are further supported by the work of *Néel (1948)* and *Brockhouse and Watanabe (1963)*. The calculations performed by *Uhl and Siberchicot (1995)* give magnitudes for the exchange energies which differ from the most recent experimental work. They suggested this was due to constraints placed on the directions of spins within their calculations.

1.4.2 Maghemite

Maghemite ($\gamma\text{-Fe}_2\text{O}_3$) is a ferrimagnetic metastable iron oxide typically formed by the oxidation of magnetite, with which it is closely structurally related. It occurs naturally as a weathering product of magnetite, and has found practical use over the past 70 years as a material used in electronic recording media (*Dronskowski, 2001*).

The Curie temperature of maghemite has been historically difficult to determine, as maghemite

Table 1.1: Nearest neighbours of magnetite cations. An atom in the spinel lattice falls into one of six types, which have nearest neighbours at different locations. A site atoms can have two types of nearest neighbour locations (Set I and Set II). B_1 and B_2 atoms occupy alternate layers of the unit cell and also have two types of nearest neighbour locations each. Distances in units of $\frac{a}{8}$. Table adapted from Glasser and Milford (1963).

Nearest neighbours to an A site atom centred at $(0, 0, 0)$

	Set I		Set II	
A sites	$(\bar{2}, \bar{2}, 2)$	$(2, 2, 2)$	$(2, 2, \bar{2})$	$(\bar{2}, \bar{2}, \bar{2})$
	$(2, \bar{2}, 2)$	$(\bar{2}, 2, 2)$	$(\bar{2}, 2, \bar{2})$	$(2, \bar{2}, \bar{2})$
B_1 sites	$(\bar{1}, \bar{3}, 1)$	$(1, 3, 1)$	$(1, 3, \bar{1})$	$(\bar{1}, \bar{3}, \bar{1})$
	$(\bar{3}, \bar{1}, 1)$	$(\bar{1}, 1, \bar{3})$	$(3, 1, \bar{1})$	$(1, \bar{1}, 3)$
	$(3, 1, 1)$	$(1, \bar{1}, \bar{3})$	$(\bar{3}, \bar{1}, \bar{1})$	$(\bar{1}, 1, 3)$
B_2 sites	$(1, 1, 3)$	$(1, \bar{3}, \bar{1})$	$(\bar{1}, \bar{1}, \bar{3})$	$(\bar{1}, 3, 1)$
	$(\bar{1}, \bar{1}, 3)$	$(\bar{1}, 3, \bar{1})$	$(1, 1, \bar{3})$	$(1, \bar{3}, 1)$
	$(3, \bar{1}, \bar{1})$	$(\bar{3}, \bar{1}, \bar{1})$	$(\bar{3}, 1, 1)$	$(3, 1, 1)$

Nearest neighbours to an B_1 site atom centred at $(0, 0, 0)$

	Set I		Set II	
A sites	$(\bar{3}, \bar{1}, 1)$	$(1, \bar{1}, \bar{3})$	$(3, 1, 1)$	$(\bar{1}, 1, \bar{3})$
	$(\bar{1}, \bar{3}, \bar{1})$	$(1, 3, 1)$	$(1, 3, \bar{1})$	$(\bar{1}, \bar{3}, 1)$
	$(3, 1, \bar{1})$	$(\bar{1}, 1, 3)$	$(\bar{3}, \bar{1}, \bar{1})$	$(1, \bar{1}, 3)$
B_1 sites	$(2, \bar{2}, 0)$	$(\bar{2}, 2, 0)$	$(2, \bar{2}, 0)$	$(\bar{2}, 2, 0)$
B_2 sites	$(\bar{2}, 0, \bar{2})$	$(0, \bar{2}, 2)$	$(\bar{2}, 0, 2)$	$(0, \bar{2}, \bar{2})$
	$(2, 0, 2)$	$(0, 2, \bar{2})$	$(2, 0, \bar{2})$	$(0, 2, 2)$

Nearest neighbours to an B_2 site atom centred at $(0, 0, 0)$

	Set I		Set II	
A sites	$(3, \bar{1}, \bar{1})$	$(\bar{1}, \bar{1}, 3)$	$(\bar{3}, 1, \bar{1})$	$(1, 1, 3)$
	$(1, \bar{3}, 1)$	$(\bar{1}, 3, \bar{1})$	$(\bar{1}, 3, 1)$	$(1, \bar{3}, \bar{1})$
	$(\bar{3}, 1, 1)$	$(1, 1, \bar{3})$	$(3, \bar{1}, 1)$	$(\bar{1}, \bar{1}, \bar{3})$
B_1 sites	$(2, 0, 2)$	$(0, 2, 2)$	$(\bar{2}, 0, 2)$	$(0, \bar{2}, 2)$
	$(\bar{2}, 0, \bar{2})$	$(0, \bar{2}, \bar{2})$	$(2, 0, \bar{2})$	$(0, 2, \bar{2})$
B_2 sites	$(\bar{2}, \bar{2}, 0)$	$(2, 2, 0)$	$(\bar{2}, \bar{2}, 0)$	$(2, 2, 0)$

inverts to the weakly magnetic rhombohedral hematite (α -Fe₂O₃) when heated. This inversion has been reported to occur at many different temperatures over the range 523-1023K (Dunlop and Özdemir, 1997). A number of different methods to estimate the Curie temperature of maghemite

Table 1.2: Nearest neighbour exchange energies in magnetite

Author	J_{AA} meV	J_{AB} meV	J_{BB} meV
<i>Brockhouse and Watanabe (1963)</i>		-2.3	
<i>Bourdonnay et al. (1971)</i>	-1.56	-2.38	0.26
<i>Möglestue (1968)</i>	-1.52	-2.42	0.31
<i>Néel (1948)</i>	-1.5	-2.0	0.04
<i>Uhl and Siberchicot (1995)</i>	-0.11	-2.92	0.63

have been employed, typically yielding a value of $T_C \approx 950\text{K}$. In contrast to magnetite, it does not undergo low-temperature crystallographic transition.

Structure

Maghemite exhibits a spinel crystal structure with a lattice constant of $a = 8.347\text{\AA}$ (*Shmakov et al.*, 1995). However, unlike magnetite, all iron atoms are in a trivalent state (Fe^{3+}). In order to meet the requirements of charge neutrality, this necessitates the formation of lattice site vacancies. The maghemite structure can be obtained by introducing 8/3 vacancies out of the 24 Fe atoms in the cubic unit cell where vacancies are known to occupy the octahedral sites. The measured moment of maghemite is $2.38\mu_B$ per formula unit close to the theoretical moment of $2.5\mu_B$ (*Henry and Boehm*, 1956).

The precise details of the full structure of maghemite have taken a number of years to resolve. *Braun* (1952) noticed that maghemite possesses the same $P4_332$ superstructure as lithium ferrite (LiFe_5O_8), in which Li atoms are restricted to the 4b Wyckoff positions. In maghemite, the same symmetry exists if the vacancies are restricted the 4b Wyckoff sites, with an added level of disorder created by a requirement of 1/3 occupancy of the 4b sites. Further studies by *Van Oosterhout and Rooijmans* (1958), *Greaves* (1983) and *Shmakov et al.* (1995) have shown that the full superstructure of maghemite is a tetragonal spinel, where $c = 3a$. This structure possesses a higher level of order than the $P4_332$ structure, most likely the $P4_12_12$ spacegroup, describing fully ordered maghemite. In this configuration, no two adjacent layers in the c direction contain occupied 4b sites (Figure 1.9). A DFT study of maghemite vacancy ordering considered all 29 inequivalent vacancy combinations which possess the lower symmetry $P4_332$ structure (*Grau-Crespo et al.*, 2010). Only one of the 29 combinations was found to possess the $P4_12_12$ spacegroup. This structure corresponded to the fully ordered vacancy configuration and was the most energetically stable vacancy configuration. It therefore appears highly likely that the preferred structure of maghemite is one with fully ordered vacancies.

It is still not clear under which circumstances vacancy disorder may arise. It has been suggested that maghemite nanoparticles exhibit vacancy disorder (*Bastow et al.*, 2009); however, previous

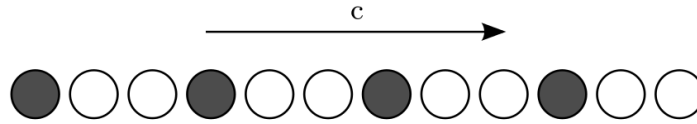


Figure 1.9: Vacancy ordering in maghemite with the $P4_12_12$ spacegroup. There are 12 layers of B site atoms in the c direction of the full tetragonal supercell. On each of these layers there is a single $4b$ Wyckoff position, which are represented in this figure by the grey and white circles. $4b$ positions that are occupied are shown as grey circles, whilst unoccupied sites are shown as white circles. The fully-ordered vacancy structure can be seen in which no two adjacent layers contain occupied $4b$ sites.

experiments on small maghemite needles suggested that an ordered structure is preserved down to 30 nm length scales (Somogyvári *et al.*, 2002). Surface effects may also alter the preferred cation distribution of atoms on the surface, as has been seen in magnetite (Bliem *et al.*, 2014), which in small systems make up an important fraction of the total particle.

Exchange Energies

To my knowledge, the exchange energies of maghemite have yet to be estimated by either experimental or *ab initio* methods. However, there have been two studies in which maghemite nanoparticles were modelled using atomistic techniques (Kodama, 1999; Iglesias and Labarta, 2001). In both cases, the authors used estimates of exchange energies for $\text{Fe}^{3+}\text{-O-Fe}^{3+}$ linkages in the inverse spinel nickel ferrite (NiFe_2O_4), which were found to have values of $J_{AA} = -1.8$ meV, $J_{AB} = -2.4$ meV and $J_{BB} = -0.7$ meV. However, it should be noted that both the lack of vacancies in nickel ferrite, and the presence of Ni^{2+} ions, are likely to cause some unknown quantity of change to the values of J_{ij} , and so can only be considered a first approximation of exchange energies in maghemite.

1.4.3 Micron and nanoscale magnetite-maghemite particles

Oxidation of magnetite to maghemite in fine particles

The oxidation of magnetite initially occurs at the surface, where Fe^{2+} ions are either partially removed from the crystal or react with oxygen and are converted to Fe^{3+} to form a new crystal layer (O'Reilly, 1984). Thereafter, Fe^{2+} ions diffuse to the surface where they oxidise and lead to growth of the particle (Sidhu *et al.*, 1977). Models of diffusion have been applied to the kinetics of the low temperature oxidation of micron sized Fe_3O_4 particles by solving Fick's second equation to obtain the diffusion constant, D (Gallagher *et al.*, 1968; Sidhu *et al.*, 1977). Recent experiments on the oxidation of nanoscale Fe_3O_4 particles in air over a period of three years, have revealed

that significant differences in the value of D , and hence diffusion rates, are seen in particles with differing synthesis procedures (*Bogart et al.*, 2018).

Magnetite-maghemite core-shell particles

The low temperature partial oxidation of magnetite to maghemite in micro and nano sized particles creates a particle with a steep oxidation gradient (*Gallagher et al.*, 1968; *Askill*, 1970). This process creates a core-shell structure with a core of stoichiometric magnetite and a shell of maghemite, which has been verified in particles ranging from 40 nm to 0.5 μm in size (*Sidhu et al.*, 1977; *Daou et al.*, 2006).

Micromagnetic modelling of magnetite-maghemite core-shell particles investigated the effect of the core-shell structure and increasing maghemisation on the hysteresis properties of particles 40-250 nm in diameter (*Ge et al.*, 2014). Results showed that the coercivity, B_C , of 40 and 60 nm single domain particles decreases with increasing oxidation/shell thickness but that larger, pseudo-single domain, particles showed less variation in B_C with oxidation.

Characterising magnetite-maghemite particles of sizes less than 40 nm is technically challenging, and studies have yielded conflicting results as to the composition of such particles. *Santoyo Salazar et al.* (2011) found that particles greater than 20 nm have a core-shell structure with a core of stoichiometric magnetite and a shell of maghemite. For particles of 10 nm in diameter, they concluded that pure magnetite was not present, and that some level of oxidation had occurred throughout the particle. In contrast, *Frison et al.* (2013) found that magnetite-maghemite nanoparticles of 10 nm may contain up to 50% stoichiometric magnetite, and concluded that a core-shell structure was therefore likely.

1.5 Thesis layout

The following chapters of this thesis use numerical modelling techniques to investigate the effect of size and shape on the Curie temperature of magnetic nanoparticles and the effect of surface oxidation on the magnetic properties of magnetite-maghemite core-shell nanoparticles.

Chapter 2 discusses the three modelling techniques used throughout this thesis. The development, implementation and testing of a numerical mean-field model is presented. The background of the Wien2k density functional theory (DFT) code is presented, and the specific challenges related to estimating exchange energies in iron-oxides using DFT are considered and tested. Finally the implementation and testing of a classical Heisenberg Monte Carlo model is discussed.

In Chapter 3, the mean-field model is applied to model magnetic nanoparticles across a range of crystal structures and shapes. The effect of size and shape on the Curie temperature of these particles is investigated.

Attempts to estimate the principal exchange energies in magnetite and maghemite using den-

sity functional theory are discussed in Chapter 4. Estimates for the exchange energies are obtained for magnetite and are compared to the results of previous studies. Difficulties in obtaining estimates for maghemite are discussed.

The Monte Carlo model is used to model magnetic nanoparticles in Chapter 5. The model is initially applied to systems of nanoparticles with the same crystal structures and shapes as studied in Chapter 3. Comparisons between the results of the mean-field and Monte Carlo approaches are drawn. Magnetite-maghemite core-shell particles are modelled, with the effect of increasing oxidation of the magnetite core on Curie temperature and hysteresis properties investigated.

Chapter 6 presents the conclusions of this thesis and discusses avenues for future research.

Chapter 2

Modelling methods

In this chapter, the three modelling methods used in this thesis are discussed. The mean-field model (section 2.1) is used in Chapter 3, the density functional theory code Wien2k (section 2.2) is used in Chapter 4 and the Monte Carlo model (section 2.3) is used in Chapter 5. The mean-field model and Monte Carlo model were written by myself, and Wien2k is written and maintained by Peter Blaha and co-workers (*Blaha et al.*, 2018).

2.1 Mean-field modelling

2.1.1 The mean-field approximation

The mean-field approximation is a well understood method for analysing the behaviour of magnetic systems, having been successfully applied across the spectrum of magnetic models from the Ising model to spin glasses (*Mezard et al.*, 1987; *Christensen and Moloney*, 2005). It considers only the effect of a local average field by ignoring correlations between fluctuations in the spins of the system. In the Heisenberg model the Hamiltonian (*Fisher*, 1964),

$$\mathcal{H} = -2 \sum_{\langle ij \rangle} J_{ij} S_i S_j - g \mu_B h \sum_{i=1}^N S_i, \quad (2.1)$$

is first expanded in terms of fluctuations away from the average spin (*Christensen and Moloney*, 2005),

$$\delta_i = S_i - \langle S_i \rangle, \quad (2.2)$$

before neglecting the effect of time-averaged correlations between them,

$$\langle \delta_i \delta_j \rangle = 0. \quad (2.3)$$

In bulk systems, such as the elemental ferromagnets, this leads to a self-consistent expression for the normalised magnetisation, $m = \langle S \rangle / S$ in terms of the Brillouin function (*Chikazumi*, 2010),

$$m = B_S \left(\frac{2S^2 J z m}{k_B T} \right) \quad (2.4)$$

where S is the spin of the system, J is the exchange energy, z is the number of nearest neighbours and,

$$B_S(x) = \frac{2S+1}{2S} \coth \left(\frac{2S+1}{2S} x \right) - \frac{1}{2S} \coth \left(\frac{1}{2S} x \right). \quad (2.5)$$

In the model considered here, mean-field theory is applied to a system of Heisenberg spins in which each site is considered to be unique. This leads to the generalised mean-field equations,

$$m_i = B_{S_i} \left(S_i \frac{\sum_{j \in N_i} 2J_{ij} S_j m_j + g\mu_B h}{k_B T} \right), \quad (2.6)$$

where m_i is the normalised magnetisation of site i , S_i is the spin at site i , B_{S_i} is the Brillouin function, J_{ij} is the isotropic exchange interaction between sites i and j defined such that ferromagnetic exchange is positive, $g \approx 2$ is the gyromagnetic ratio (*Odom et al.*, 2006), μ_B is the Bohr magneton, h is an external magnetic field acting on each site, k_B is the Boltzmann constant, and T is temperature. The sum over j acts over the set of nearest neighbours of i , where $N_i := \{j : J_{ij} \neq 0\}$. Each site i is a spin in the system being studied, so can represent the unique atoms in a complex crystal lattice (*Fabian et al.*, 2015), the layers in a thin film (*Jensen et al.*, 1992), or, as in the case being studied here, the atoms in a magnetic nanoparticle. Due to a discrepancy which arises between the derivation presented by *Fabian et al.* (2015) and the result in (2.6), a full derivation of the mean-field equations is given in Appendix A.

2.1.2 Solving coupled non-linear equations

The generalised mean-field equations form a set of n coupled non-linear equations. The solutions to these equations are not analytically tractable and so a numerical approach must be taken to solving them. By re-casting (2.6) as,

$$f_i = B_{S_i} \left(S_i \frac{\sum_{j \in N_i} 2J_{ij} S_j m_j + g\mu_B h}{k_B T} \right) - m_i = 0, \quad (2.7)$$

the task of solving the equations is transformed into a root finding problem, in which the solution to the set of equations f_i is the set of variables m_i , the magnetisation of each site. There is normally more than a single solution to such systems of equations, so further conditions must be fulfilled by the desired solution. In the case of the mean-field equations, the trivial root $m_i = 0$ is not a valid solution below T_C , when it falls at a maximum of free energy. In addition, m_i are normalised magnetic moments, i.e., they must lie in the range $-1 \leq m_i \leq 1$.

The solutions to a system of non-linear equations are usually obtained by an n dimensional Newton-based method (*Press et al.*, 2007). A set of equations such as those in equation (2.7) may be considered elements of the vector $\mathbf{f}$,

$$\mathbf{f}(\mathbf{x}) = 0. \quad (2.8)$$

where $\mathbf{f}$ is the vector of equations f_i and $\mathbf{x}$ is the vector of variables x_i (in (3.3) $x_i = m_i$). Close to $\mathbf{x}$, f_i can be expressed in the form of a Taylor expansion,

$$f_i(\mathbf{x} + \delta\mathbf{x}) = f_i(\mathbf{x}) + \sum_{j=1}^N \frac{\partial f_i}{\partial x_j} \delta x_j + \mathcal{O}(\delta\mathbf{x}^2), \quad (2.9)$$

where the partial derivatives $\mathcal{J}_{ij} = \frac{\partial f_i}{\partial x_j}$ form the Jacobian matrix $\mathbf{J}$. Neglecting second order (and higher) terms of the expansion, and setting $f_i(\mathbf{x} + \delta\mathbf{x}) = 0$, a set of linear equations for the correction to $\mathbf{x}$ are obtained,

$$\mathbf{J} \cdot \delta\mathbf{x} = -\mathbf{f}(\mathbf{x}), \quad (2.10)$$

which can be solved using methods such as QR or LU decomposition to obtain $\delta\mathbf{x}$ (*Trefethen and Bau*, 1997). $\mathbf{x}$ is then iteratively updated according to,

$$\mathbf{x}_{k+1} = \mathbf{x}_k + \delta\mathbf{x}_k \quad (2.11)$$

until the desired level of convergence is reached for either $\mathbf{f}$ or $\mathbf{x}$. There may be many roots to the system of equations being solved, and finding the desired root is highly dependent upon the initial guess, $\mathbf{x}_0$. Furthermore, the sensitivity to the initial condition is such that the base algorithm can fail to converge entirely. Therefore, it is necessary to constrict the initial guess and range of acceptable $\mathbf{x}_{\text{final}}$ values as closely as possible (*Press et al.*, 2007).

Globally convergent methods

In the basic Newton method, the step $\delta\mathbf{x}$ is always accepted, and the user must hope it leads to convergence of the solutions. In order to improve the performance of this approach, the Newton method can be adapted to ensure there is always some progression towards a root with each step. There is still no guarantee that these methods will succeed, but it is more likely than the basic approach. Two common adaptations to the Newton method are the line search and trust region algorithms, discussed below.

The line search algorithm begins by taking a full Newton step. This is desirable, as once close enough to the solution, the algorithm will experience quadratic convergence. However, in the line search method the Newton step, $\delta\mathbf{x}$, is restricted by requiring any step to also decrease $|\mathbf{f}|^2 = \mathbf{f} \cdot \mathbf{f}$ (*Press et al.*, 2007). By defining,

$$F = \frac{1}{2} \mathbf{f} \cdot \mathbf{f}, \quad (2.12)$$

it is possible to show that the condition imposed on the Newton step will also minimise F . Therefore, every solution to $\mathbf{f} = 0$ is a local minimum of F . Crucially, the reverse is not true, local minima of F exist where $\mathbf{f} \neq 0$, which prevents minimisation algorithms being employed to find roots. Should the initial step not reduce the value of F , the algorithm backtracks along the direction of $\delta \mathbf{x}$ until a step that does reduce F is found. Because $\delta \mathbf{x}_k$ is a direction of descent for F_k , the algorithm is guaranteed to be able to reduce F for some small step $\delta \mathbf{x}$. As $\mathbf{f} = 0$ is a minimum of F , the solution of the system of equations will eventually be found. The method will fail if it finds a minimum of F in the direction of $\delta \mathbf{x}$ that is not also a solution to $\mathbf{f} = 0$, however re-initialising the problem with a different initial guess often leads to the desired solution being found.

The trust region algorithm works by creating an approximate model to the functions f_i and testing this model within a trust region around the last iterated point (*Conn et al.*, 2000). At each iterated x_k , a model, $m_k(x)$, is defined which generally has a quadratic form, e.g. a second order Taylor series expansion of f at x_k . The trust region is the set of all points that lies within,

$$\|x - x_k\|_k \leq \Delta_k. \quad (2.13)$$

A trial step, s_k , is made to the point $x_k + s_k$, which must both sufficiently reduce the model and satisfy the bound $\|s_k\|_k \leq \Delta_k$. There are several ways of determining the step direction, s_k , the simplest being to take the direction of the Newton step $\delta \mathbf{x}$ but modifying its length to ensure it is not larger than the trust region. The step s_k must then be checked against the functions to be solved. By defining,

$$\rho_k = \frac{f(x_k) - f(x_k + s_k)}{m_k(x_k) - m_k(x_k + s_k)}, \quad (2.14)$$

as a ratio of the objective functions and the model, the trial step can be accepted based on the value of ρ_k . If the trial step is accepted, then in the next iteration the trust region is either expanded or kept the same. If the trial step is not accepted, then the trust region is made smaller and the iteration restarted.

2.1.3 PETSc

The need to numerically solve systems of non-linear equations is widespread in scientific and engineering problems, and there exist a number of numerical libraries which contain the routines needed for this task. One such library is PETSc, described as a ‘suite of scalable data structures and routines for use in scientific computation’ (*Balay et al.*, 2016). It contains methods for solving a range of computational problems such as linear and non-linear systems of equations, all in a

parallel environment. This makes it attractive to use for solving medium to large scale problems. The Scalable Non-linear Equations Solvers (SNES) component of PETSc is used here to find solutions to the mean-field equations.

SNES offers the user a range of solver options, allowing choice between line search and trust region convergence methods, control over the tolerances defining convergence, and analytic or finite difference construction of the Jacobian matrix. Additionally it provides methods to help check the accuracy of hand coded elements of the function, $\mathbf{f}$, and Jacobian.

Calculating the Jacobian

The first step of any Newton based approach is to calculate the Jacobian. From inspection of equation (2.7), it can be seen that f_i is a function of m_i and m_{j_n} , where j_n donates a nearest neighbour of site i . Therefore, the only non-zero elements of the Jacobian are $\mathcal{J}_{ii}$ and $\mathcal{J}_{ij_n}$. Taking the derivatives $\partial_{m_i} f_i$ and $\partial_{m_{j_n}} f_i$, the following expressions for the elements of the Jacobian are obtained. For $i = j$,

$$\frac{\partial f_i}{\partial m_i} = -1. \quad (2.15)$$

For $j \in N_i$,

$$\frac{\partial f_i}{\partial m_j} = \frac{2J_{ij}S_j}{k_B T} \left[\left(\frac{1}{2S_i} \right)^2 \frac{1}{\sinh^2 \left(\frac{1}{2S_i} \xi_i \right)} - \left(\frac{2S_i + 1}{2S_i} \right)^2 \frac{1}{\sinh^2 \left(\frac{2S_i + 1}{2S_i} \xi_i \right)} \right], \quad (2.16)$$

where,

$$\xi_i = \frac{\sum_{j \in N_i} 2J_{ij}S_j m_j + g\mu_B h}{k_B T}. \quad (2.17)$$

Otherwise for $i \neq j$ and $j \notin N_i$,

$$\frac{\partial f_i}{\partial m_j} = 0. \quad (2.18)$$

Hand-coding any analytic Jacobian, especially one of the potential complexity of equation (2.16), is prone to user input errors. In order to catch these errors, PETSc contains a method which compares $\mathbf{J}$ to $\mathbf{J}_{\text{FD}}$, a finite-difference approximation to the Jacobian computed from $\mathbf{f}$. SNES calculates the difference $\|\mathbf{J} - \mathbf{J}_{\text{FD}}\|$, and ratio $\frac{\|\mathbf{J} - \mathbf{J}_{\text{FD}}\|}{\|\mathbf{J}\|}$, of the analytic and finite-difference Jacobians at values of $\mathbf{x} = -\mathbf{1}$ and $\mathbf{x} = \mathbf{1}$. Values of the ratio of $\mathcal{O}(1 \times 10^{-8})$ suggest that the hand-coded Jacobian has been coded without errors (*Balay et al.*, 2016). Additionally, agreement between $\mathbf{J}$ and $\mathbf{J}_{\text{FD}}$ implicitly suggests that $\mathbf{f}$ has also been correctly computed and constructed.

The hand coded Jacobian for a test system of a simple cubic particle of size $5 \times 5 \times 5$ atoms was compared to the finite difference method computed by PETSc. At $\mathbf{x} = -\mathbf{1}$ the ratio was found to be 1.01×10^{-8} and at $\mathbf{x} = \mathbf{1}$ the ratio was 1.28×10^{-8} . These values of ratios are of the order expected for correct coding of the Jacobian.

Convergence methods

A number of Newton variant methods are provided by SNES, including line search and trust region approaches. The line search method has further options to determine how the Newton step is implemented. Pre-conditioning can also be applied to the linear solvers (termed KSP in PETSc) which solve the linear part of the Newton method, and influence the convergence of these methods (Balay *et al.*, 2016). In order to understand which set of options were the most appropriate, the time taken per iteration and the number of iterations taken to reach convergence were studied in a small test system (Table 2.1). The magnetisation of the particle was calculated for temperatures in the range 1-90 K, in steps of 1K. The overall solve time (the amount of time running the method *SNESsolve()*) for these 90 temperatures was recorded, alongside the total number of iterations.

Table 2.1: Runtime, average time per temperature step and average number of iterations per temperature step for a range of SNES solver options. Newton methods include line search and trust region approaches. Two linesearch options are used; the basic type using the full Newton step (basic) and the backtracking method (bt) discussed above. Pre-conditioning is either performed using LU factorisation or not applied (none). The test system was a $20 \times 20 \times 20$ particles with uniform spin of $S_i = 2$ and exchange energy of $J_{ij} = 3.5k_B$. The program was run on a single Intel Xeon CPU E5-2640 v3 with a speed of 2.60 GHz.

Newton method	Ls type	Pre-conditioner	Runtime (s)	<time>/step	<its>/step
Line search	basic	none	278.2	3.1	2.5
Line search	basic	pclu	473.3	5.3	2.6
Line search	bt	none	284.8	3.2	2.9
Line search	bt	pclu	498.7	5.5	3.0
Trust region		none	352.4	3.9	3.0
Trust region		pclu	432.6	4.8	2.7

Whilst the line search methods with no pre-conditioning give the fastest runtimes for the test calculation, above T_C these methods fail to converge. Running the line search methods with a LU pre-conditioner does not solve this problem and also confers a significant time penalty. The trust region algorithm converges to a solution at every time step, with or without pre-conditioning, but is 0.8 seconds slower per temperature step than the fastest line search method. In order to preserve the speed of the line search method, and the robustness of the trust region approach, the ‘basic’ line search method with no pre-conditioning was set as the default method. Should the system fail to converge, the problem was re-initialised with the trust region method with no pre-conditioning to ensure convergence.

Convergence parameters

After each iteration, SNES tests for convergence against a number of convergence parameters: the absolute convergence tolerance a_{tol} , the relative convergence tolerance r_{tol} , the convergence tolerance in terms of the norm of the change in the solution between steps s_{tol} and, in the case of a trust region method, the trust region convergence tolerance tr_{tol} . Should one of the following thresholds be reached, then the system of equations is considered to have converged to a solution.

$$\|\mathbf{f}\| < a_{\text{tol}} \quad (2.19)$$

$$\frac{\|\mathbf{f}\|}{\|\mathbf{f}_{\text{initial}}\|} < r_{\text{tol}} \quad (2.20)$$

$$\frac{\|\delta\mathbf{x}\|}{\|\mathbf{x}\|} < s_{\text{tol}} \quad (2.21)$$

PETSc defines a set of default tolerance values of $a_{\text{tol}} = 10^{-50}$, $r_{\text{tol}} = 10^{-8}$ and $s_{\text{tol}} = 10^{-8}$, which have been chosen to work well for a wide range of problems (*Balay et al.*, 2016). The convergence criteria and default values of tr_{tol} could not be obtained from either the PETSc User manual or the related online documentation (*Balay et al.*, 2016). The default tolerances were checked against a range of user defined tolerances to ensure that a sufficient level of accuracy was obtained by the defaults. The test system used was a simple cubic particle of size $20 \times 20 \times 20$ atoms in size, with uniform spin of $S_i = 2$ and exchange energy of $J_{ij} = 3.5k_B$. When testing a_{tol} , r_{tol} and s_{tol} the basic linesearch algorithm was used as it was previously identified as the preferred algorithm for solving the mean-field equations; tr_{tol} was tested using the trust region method. Each parameter was varied individually, with all other parameters held at their default values. The default values for the convergence tolerances were found to be good choices, with $\Delta m = m - m_{\text{default}}$ varying very little as the tolerances were changed (Figure 2.1).

2.1.4 Development of the numerical model

Calculating $\mathbf{m}$, $\mathbf{f}$ and $\mathbf{J}$

In order to solve the mean-field equations PETSc requires: (1) the initial guess for the vector of magnetisations, $\mathbf{m}$, (2) the value of the function $\mathbf{f}(\mathbf{m})$, at each iteration, and (3) the value of the Jacobian, $\mathbf{J}$, at each iteration, to be passed to it.

Whilst the initial guess for $\mathbf{m}$ can easily be made, evaluating $\mathbf{f}$ and $\mathbf{J}$ for a given $\mathbf{m}$ is not entirely straightforward. Each element of $\mathbf{m}$, m_i , corresponds to an atom on a crystal lattice in a particle which interacts with its nearest neighbours m_j , knowledge of which are required for calculating $\mathbf{f}$ and $\mathbf{J}$. A list of nearest neighbours for each m_i is made by mapping to its position (i, j, k) in the particle, which then allows the efficient computation of $\mathbf{f}$ and $\mathbf{J}$ at each iteration.

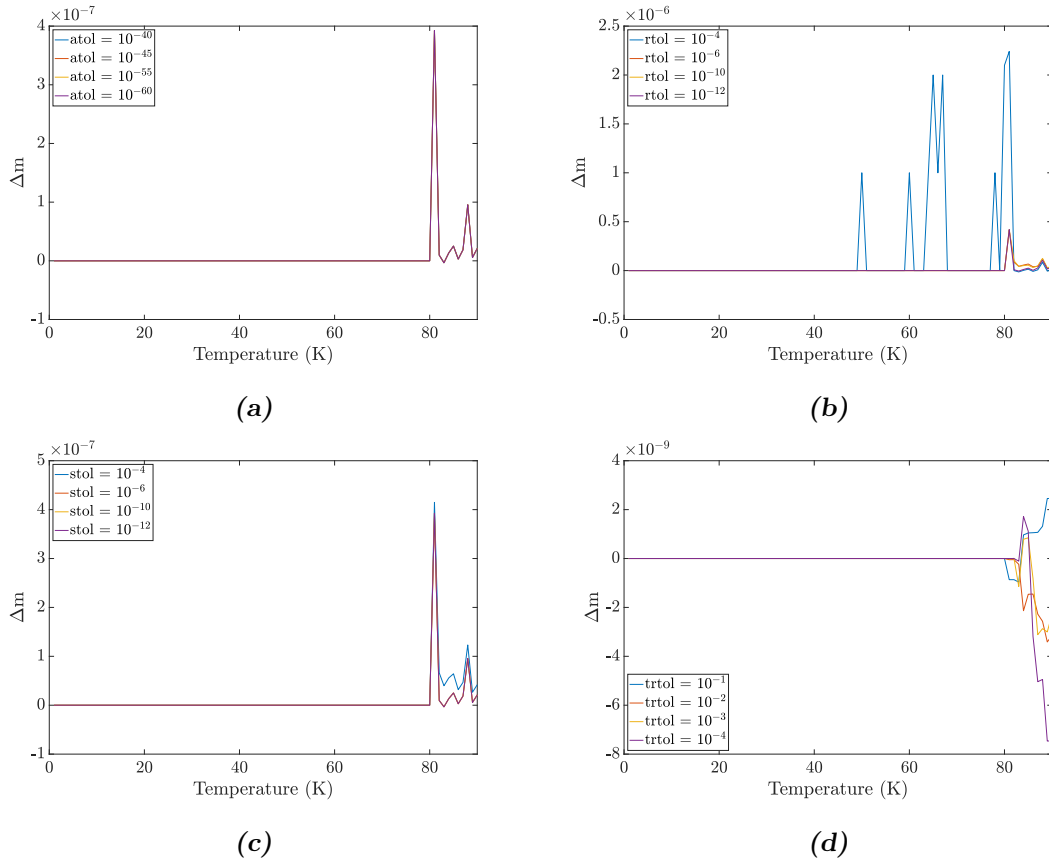


Figure 2.1: Δm for a range of tolerance values of either side of the default values; (a) a_{tol} , (b) r_{tol} , (c) s_{tol} and (d) tr_{tol} . Default values are $a_{tol} = 10^{-50}$, $r_{tol} = 10^{-8}$ and $s_{tol} = 10^{-8}$.

Generating particles

Particles were modelled using simple cubic, body-centered cubic and inverse spinel (magnetite) crystal structures. For each crystal structure, five different shapes were studied: cubes, spheres, and three elongated needle-like shapes with aspect ratios of 2:1:1, 5:1:1 and 10:1:1, where each shape could be modelled over a range of sizes. Spherical particles were approximated on the crystal lattice by including an atom if it lay within $\frac{d}{2}$ of the centre of the particle.

Magnetisation curves

When the mean-field equations are solved for a particular temperature, the magnetisation at each atomic site in the crystal lattice is then known. Iterating across a range of temperatures allows magnetisation curves, magnetisation surfaces and other spatial magnetic behaviour to be investigated (Figure 2.2). After a particle has been initialised, magnetisations are found for $T = T_{\min}$. The temperature is then incremented such that $T_{\text{new}} = T_{\text{old}} + \Delta T$. The initial guess for magnetisation at the new temperature is set to $m_i = m_i(T_{\text{old}})$, as the magnetisation of each site will change little for each temperature iteration, provided ΔT is not excessively large.

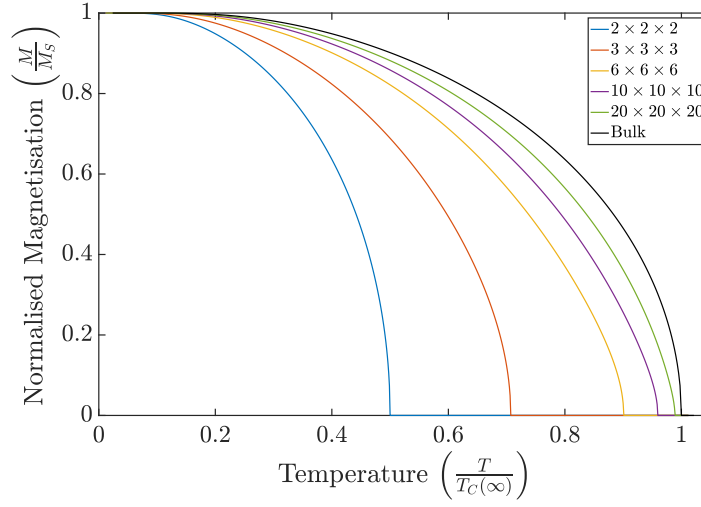


Figure 2.2: Example magnetisation curves for cubic sc nanoparticles with a uniform spin of $S_i = 2$ and isotropic exchange energy of $J_{ij} = 3.5k_B$. The magnetisation curve for the bulk system is also shown.

Determining T_C

In the mean-field approximation, the Curie temperature occurs at the point when $m_i = 0$ becomes the only solution to the system of equations described by equation (2.6), and corresponds to a change in the free energy of the system from a maximum to a minimum at $m_i = 0$. This is illustrated for the one-dimensional ferromagnetic bulk case (equation 2.4) in Figure 2.3.

A common approach taken to find T_C within the mean-field approximation is to linearise the mean-field equations and then solve the resulting matrix system (Fabian *et al.*, 2015). The linear approximation to the Brillouin function is given by,

$$B_{S_i}(S_i \xi_i) = \frac{S_i + 1}{3S_i} S_i \xi_i, \quad (2.22)$$

where,

$$\xi_i = \frac{\sum_{j \in N_i} 2J_{ij} S_j m_j + g\mu_B h}{k_B T}. \quad (2.23)$$

m_i is now linearly dependent on the nearest neighbour magnetisations m_j , and so the system of equations may be rewritten as a $n \times n$ matrix $\mathbf{A}$,

$$\mathbf{m} = \mathbf{A} \cdot \mathbf{m}. \quad (2.24)$$

Rearranging gives,

$$(\mathbf{A} - \mathbf{I}) \cdot \mathbf{m} = \mathbf{0}, \quad (2.25)$$

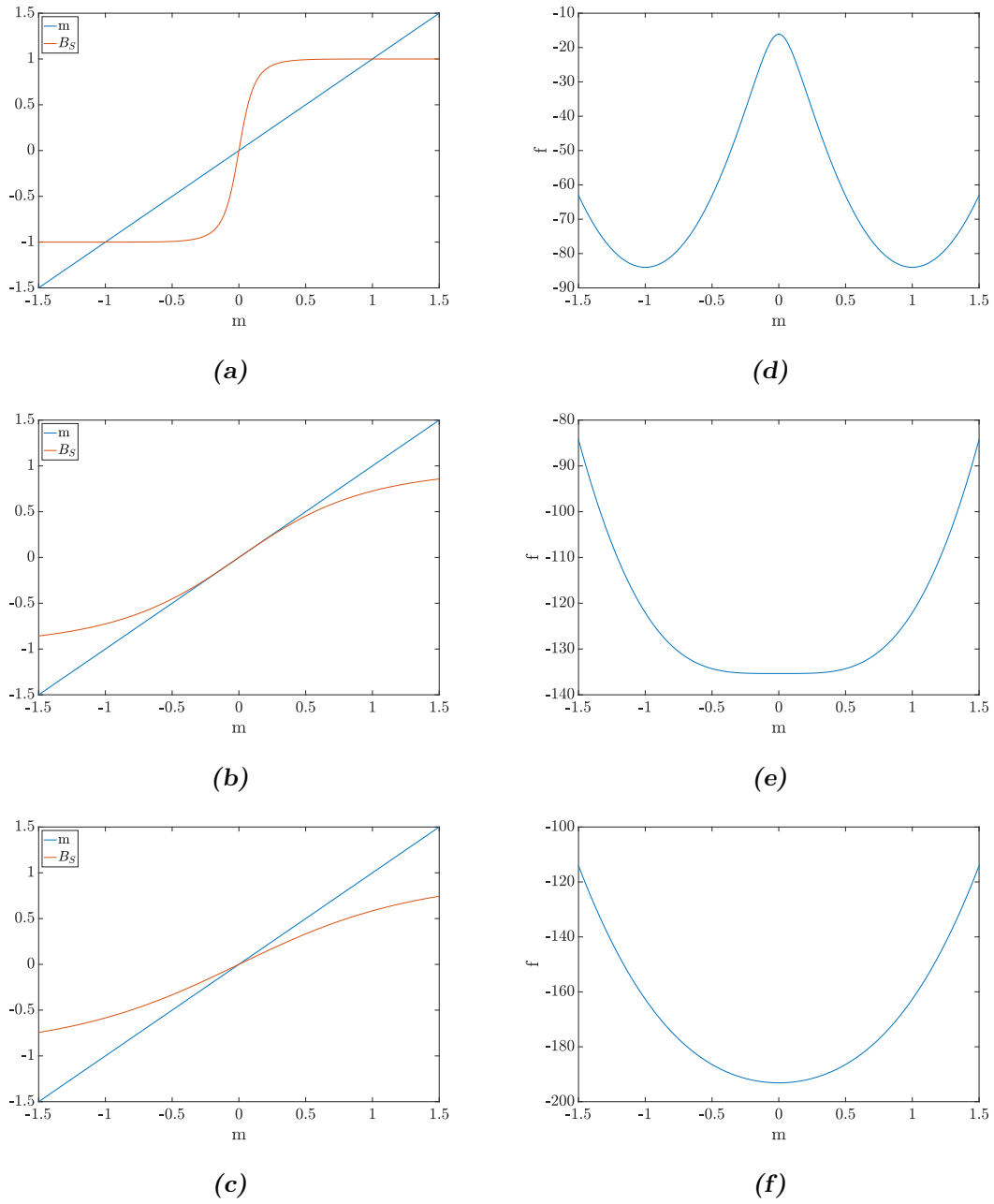


Figure 2.3: The solutions to the mean-field equation for a bulk ferromagnet shown by intersections of the two lines (see equation 2.4). For (a) $T < T_C$, (b) $T = T_C$ and (c) $T > T_C$. Corresponding free energy plots are shown in (d-f), where a minimum of the free energy is a stable physical solution.

where $\mathbf{I}$ is the identity matrix. The solution to this system of equations becomes singular at T_C and so the determinant,

$$|\mathbf{A} - \mathbf{I}| = 0, \quad (2.26)$$

where the largest real solution for T corresponds to T_C (Fabian *et al.*, 2015). Whilst this approach is successful for systems with a smaller number of unique sites, e.g., thin films and complex crystal structures, it quickly became a slow method for the nanoparticle systems studied in this model due to the size of the resulting polynomial equation which needs to be solved. An iterative method was therefore adopted in order to determine T_C from the numerical solution of equation (2.6).

The solution to the mean-field equations gives the magnetisation of each atom in the particle for a given temperature, T . Below T_C , this gives a non-zero value of magnetisation for each site and for $T \geq T_C$, magnetisation at each site is zero. It is therefore possible to determine T_C through a bisection algorithm. Two initial temperatures were chosen, $T_L = 1$ K and $T_H > T_C(\infty)$. The magnitude of the average magnetisation of the particle, $|\langle m_i \rangle|$, at the midpoint between these two temperatures,

$$T_M = \frac{T_L + T_H}{2}, \quad (2.27)$$

was calculated. If $|\langle m_i \rangle|$ was found to be greater than a threshold value $\epsilon_m = 0.0001$, then T_M was assumed to be below the Curie temperature, and T_L was replaced by T_M . For $|\langle m_i \rangle| < \epsilon_m$, T_H was replaced by T_M . This process was iterated until $T_H - T_L < 0.01$ K. The Curie temperature of the particle was then taken as,

$$T_C = \frac{T_{L_f} + T_{H_f}}{2}, \quad (2.28)$$

where T_{L_f} and T_{H_f} are the final values of T_L and T_H respectively and the error in T_C is,

$$\epsilon_{\text{err}} = \frac{T_{L_f} - T_{H_f}}{2}. \quad (2.29)$$

The Curie temperature determined by the bisection method was compared to the linearised method for smaller simple cubic particles where $S_i = 2$ and $J_{ij} = 3.5k_B$ (Table 2.2). Good agreement between the two approaches, typically with a difference in T_C of the order 10^{-3} K, is seen in all cases which validates the iterative approach to this problem.

Model workflow

The high-level workflow for the mean field model is shown in Figure 2.4. First, an input file (*input.txt*) is read, which gives details of the material, aspect ratio, shape, particle sizes and algorithm (magnetisation curve or Curie temperature) to be modelled. The SNES solvers are then initiated, and the type of algorithm set. The first particle is created alongside an initial magnetisation guess $\mathbf{m}_0$, which sets all magnetisations to lie in the expected $T = 0$ K, ground-state configuration. For example, in a ferromagnetic system all magnetisations would have a value of $m_i = 1$.

Depending on user selection, the T_C or magnetisation curve algorithm is then run. At each temperature step data are output to file after a solution is found. Additional information about

Table 2.2: Comparison of T_C of simple cubic particles, where $S_i = 2$ and $J_{ij} = 3.5k_B$, from the iterative method and linear approximation method. T_C is given here to four significant figures, but is calculated to a greater accuracy by the numerical methods. The value of ΔT_C is given to two significant figures.

Particle size	T_C (K) iterative	T_C (K) linear	ΔT (K)
2	42.00	42.00	-0.0010
4	67.96	67.96	0.0017
6	75.68	75.68	0.0022
8	78.93	78.93	-0.0022
10	80.60	80.60	0.0023
12	81.56	81.56	0.0021
14	82.16	82.16	-0.00025
16	82.57	82.57	0.0019
18	82.86	82.85	0.011
20	83.06	83.06	-0.0013

the details of the SNES solver is also recorded, i.e., details on the convergence of the SNES solvers, number of iterations. Once $T_{\max}$ or T_C is reached a new particle of different size is created, along with an initial guess, until all particle sizes have been modelled.

2.2 Density functional theory

2.2.1 Theoretical background of DFT

Density functional theory (DFT) is based on a theory developed by *Hohenberg and Kohn* (1964) and *Kohn and Sham* (1965) that showed that the time-independent Schrödinger equation can be rewritten such that the energy can be expressed as a functional of the electron density. From a practical perspective this is significant, as the Schrödinger equation can only be solved analytically for systems with one electron and numerical approaches to many electron systems have been hampered by the difficulty and huge computational cost of treating these systems (*Motta et al.*, 2017). From the Hohenberg-Kohn theorem the ground state energy, E , can be written (*Hohenberg and Kohn*, 1964),

$$E = T + U + V_{\text{nuc}} + E_{\text{XC}}[\rho] \quad (2.30)$$

where T is the kinetic energy, U is the Hartree energy, V_{nuc} is the potential energy due to nuclei, ρ is the electron density, and $E_{\text{XC}}[\rho]$ is the exchange-correlation energy, which is defined to make the above expression exact. The Kohn-Sham (KS) equations then give the wavefunctions, $\psi_i(\mathbf{r})$,

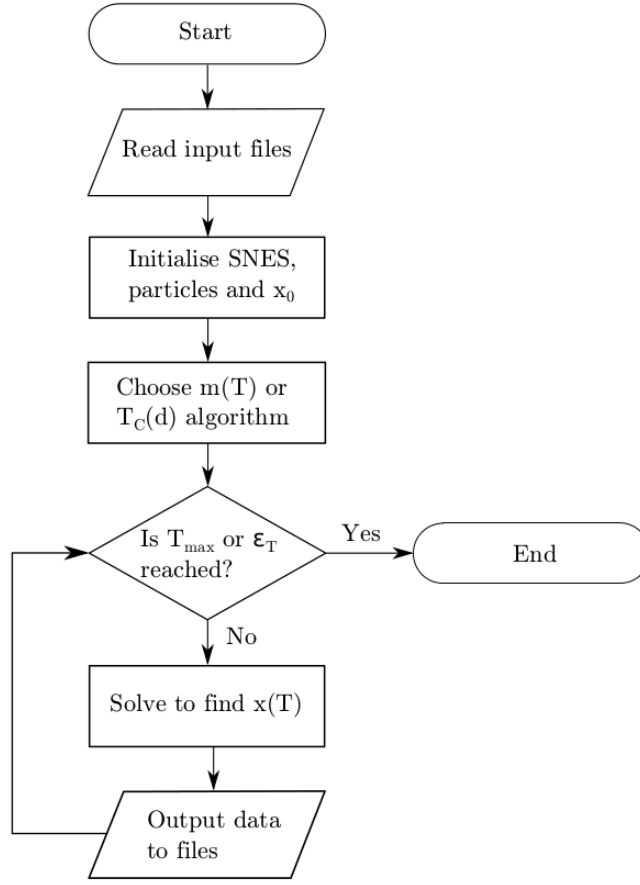


Figure 2.4: Outline of the mean field numerical algorithm.

which minimise the energy (*Kohn and Sham, 1965*),

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V_H(\mathbf{r}) + V_{\text{nuc}}(\mathbf{r}) + V_{\text{XC}}[\rho](\mathbf{r}) \right] \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}), \quad (2.31)$$

where $V(\mathbf{r})$ is the nuclear potential, $V_H(\mathbf{r})$ is the Hatree potential defined as (*Fiolhais et al., 2003*),

$$V_H(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3 r', \quad (2.32)$$

and V_{XC} is the exchange-correlation potential. If the exchange-correlation functional is known exactly, then the KS equations describe the system exactly, without having to calculate the electron-electron interaction directly. However, an exact expression for V_{XC} is unknown, and so a good approximation is crucial for reliable applications (*Jones, 2015*). Early DFT calculations employed the local density approximation (LDA), where the exchange-correlation functional is approximated using the local electron density. However, this approach has limitations in magnetic materials,

and modern calculations on materials frequently employ the generalised gradient approximation (GGA) where the exchange-correlation potential is written as a function of the local density of spin up and spin down electrons, plus the local gradients of those densities (*Perdew, 1986; Burke, 2012*). The Perdew-Burke-Ernzerhof (PBE) functional used in this study is one of the most widely used of the GGA functionals (*Perdew et al., 1996*).

The electron density can be calculated from the wavefunctions (*Payne et al., 1992*),

$$\rho(\mathbf{r}) = 2 \sum_i |\psi_i(\mathbf{r})|^2. \quad (2.33)$$

This leads to a circular problem, as the KS equations require knowledge of the electron density to compute the wavefunctions. In practice, a trial electron density is proposed and the system is iterated under a scheme which calculates a new electron density by first solving the KS equations, until the change in the electron density between iterations is below an accepted threshold. In crystalline materials, the basis set from which the wavefunctions are constructed is best described by plane waves, as their periodicity can be matched to the periodicity of the crystal structure (*Payne et al., 1992*). Close to an atomic nucleus the electron density changes rapidly over short length scales, which requires high frequency plane waves to be included as part of the basis set in order to accurately describe the electron behaviour in this region (*Schwarz et al., 2002*). This is a computationally expensive task, and so alternative approaches, such as pseudo-potentials (e.g. *Louie et al., 1982*) or alternative basis sets must be used to describe electron density close to atom nuclei (e.g. *Slater, 1937*).

In transition metal oxides such as those considered in this study, the standard approximations cause the *d*-electrons to become too de-localised, leading to incorrect descriptions of the material (*Burke, 2012*). The Hubbard potential, U , is commonly used to correct for this greater degree of de-localisation by applying a potential to the affected electrons (*Anisimov et al., 1991*). GGA+ U calculations have been successful, but the value of U is a free parameter and in a given material must be determined by comparison to experimental results. Values of $U \approx 4$ eV have been found to give good results in iron oxides (*Grau-Crespo et al., 2010; Bliem et al., 2014*), whilst studies of greigite have used a value of $U = 1.0$ eV (*Roldan et al., 2013*).

2.2.2 Wien2k

Wien2k is one of the many codes available for performing electronic structure calculations using DFT, and has been in development since its original release as ‘Wien’ in 1990 (*Blaha et al., 1990*). It is based on the full-potential linearised augmented plane-wave (LAPW) + local orbitals (lo) method which is one of the most accurate methods for applying DFT to crystals. Wien2k is used in this thesis to estimate magnetic exchange energies of iron oxides having been successfully used for this purpose on other 3d transition metal oxides, e.g., cupric oxide (*Rocquefelte et al., 2010*) and hematite-ilmenite systems (*Nabi et al., 2010*). In March 2017 I spent one month working

with Peter Blaha in the Theoretical Chemistry group at the Vienna University of Technology, where I learnt how to use Wien2k. Calculations were performed on the Imperial College HPC facility.

Wien2k introduces a basis set which is adapted to the problem of solving DFT on crystal structures. The unit cell is divided into a set of non-overlapping spheres centred at the atomic sites separated by an interstitial region (Figure 2.5), with each region using a different basis set. Inside each atomic sphere the basis set is a linear combination of radial functions multiplied by spherical harmonics (*Blaha et al.*, 2018),

$$\phi_{k_n} = \sum_{lm} [A_{lm} u_l(r, E_l) + B_{lm} \dot{u}_l(r, E_l)] Y_{lm}(\hat{r}), \quad (2.34)$$

where $u_l(r, E_l)$ is the regular solution to the radial Schrodinger equation for energy E_l , $\dot{u}_l(r, E_l)$ is the energy derivative of u_l taken at E_l , $Y_{lm}(\hat{r})$ is a spherical harmonic and A_{lm} and B_{lm} are determined by requiring that the basis function matches the corresponding basis function of the interstitial region in value and slope at the boundary. Additional basis functions called local orbitals are also added to improve the flexibility of the basis set (*Blaha et al.*, 2018),

$$\phi_{lm}^{LO} = [A_{lm} u_l(r, E_{1,l}) + B_{lm} \dot{u}_l(r, E_{1,l}) + C_{lm} u_l(r, E_{2,l})] Y_{lm}(\hat{r}), \quad (2.35)$$

where A_{lm} , B_{lm} and C_{lm} are determined by the requirement that ϕ^{LO} is normalised and has zero value and gradient at the sphere boundary. The energies for the local orbitals, $E_{1,l}$ and $E_{2,l}$, are usually chosen such that $E_{1,l}$ corresponds to a semi-core state and $E_{2,l}$ to a valence state. In the interstitial region the basis set is given by a plane wave expansion (*Blaha et al.*, 2018),

$$\phi_{k_n} = \frac{1}{\sqrt{\omega}} e^{i\mathbf{k}_n \cdot \mathbf{r}}. \quad (2.36)$$

where ω is the unit cell volume, $\mathbf{k}_n = \mathbf{k} + \mathbf{K}_n$, $\mathbf{k}$ is the wave vector inside the first Brillouin zone and $\mathbf{K}_n$ are the reciprocal lattice vectors. The solutions to the KS equations are expanded in this combined set of LAPW's according to (*Blaha et al.*, 2018),

$$\psi_k = \sum_n c_n \phi_{k_n}, \quad (2.37)$$

where the coefficients c_n are determined by the Rayleigh-Ritz variational principle. Further details and background to the LAPW + lo method and its implementation alongside the related augmented plane wave (APW + lo) method in Wien2k are beyond the scope of this thesis and can be found in the Wien2k User Manual (*Blaha et al.*, 2018) and the references found therein.

2.2.3 Optimising Wien2k calculations

Wien2k contains a number of parameters and options which must be tested and optimised to obtain an accurate result. To ensure the reliability of a given calculation, convergence of the total

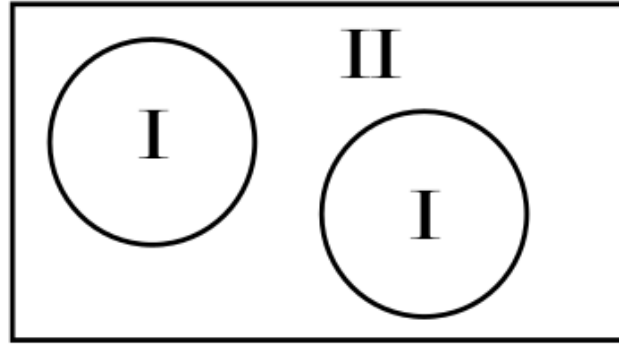


Figure 2.5: Schematic of the two regions of the unit cell for the Wien2k basis set. In the spherical region (I) the basis set is described by a linear combination of radial functions multiplied by spherical harmonics (equations 2.34). In the interstitial region (II) the basis set is described by the plane wave expansion in equation (2.36).

energy should be obtained for these variable parameters.

k-points

A bulk solid effectively contains an infinite number of electrons, a problem which must be overcome to successfully model materials using DFT. Bloch's theorem (*Bloch*, 1929) changes this problem to one of calculating a finite number of electron wavefunctions at an infinite number of k-points in reciprocal space (*Payne et al.*, 1992). However, the wavefunctions at k-points close together will be almost identical, and so it is possible to represent wavefunctions over a region of k-space by the wavefunctions at a single k-point (*Payne et al.*, 1992). A number of methods have been devised for obtaining accurate approximations to the electronic potential by calculating the electronic states at a special set of k-points in the Brillouin zone (e.g. *Monkhorst and Pack*, 1976; *Evarestov and Smirnov*, 1983; *Blöchl et al.*, 1994). Wien2k uses the improved tetrahedron method devised by *Blöchl et al.* (1994). These methods allow for an accurate approximation of an insulator or semiconductor using a very small number of k-points. Metallic systems require a denser set of k-points to accurately describe the Fermi surface. In Wien2k the number of k-points used in a calculation is provided by the user as an input. The system is more accurately described when more k-points are used, but at a computational cost proportional to the number of k-points. Eventually, the addition of further k-points leads to a negligible change in the total energy and convergence is reached. This convergence of energy with respect to the number of k-points should be observed to verify that the system of interest is being accurately described.

RK_{max}

Wien2k defines the parameter $RK_{\max}$ as (*Blaha et al.*, 2018),

$$RK_{\max} = R_{\text{MT}} \times K_{\max}, \quad (2.38)$$

where R_{MT} is the smallest atomic sphere radius of the system (region I in figure 2.5) and $K_{\max}$ is the largest k-vector of the plane wave expansion of the wavefunction (equation 2.37). $RK_{\max}$ thus controls the size of the basis set in number of plane waves and so the accuracy of the calculation. The size of the basis set scales with $(RK_{\max})^3$ and so an increase in the value of $RK_{\max}$ of 10% leads to an increase of the size of the basis set of 30% and computing time by a factor of two (*Blaha et al.*, 2018). The value of $RK_{\max}$ required for a given calculation depends on the element of the atom which has the smallest R_{MT} and the desired accuracy of the calculation. In parallel with the k-point testing, convergence of total energy with respect to $RK_{\max}$ should be observed during preliminary calculations.

Structural optimisation

DFT calculations can also be used to calculate the equilibrium geometry of a structure. Geometry optimisation is performed by calculating the forces on each atom of the input cell (which are calculated as a derivative of the energy with respect to the atomic positions). Atom positions are moved in the direction of the energy gradient and, in Wien2k, a trust-region Quasi-Newton method (*Gay*, 1983) is used to minimise the total energy (with respect to atomic position) (*Blaha et al.*, 2018). Geometry optimisation methods impose a significant time penalty on DFT calculations, as many more iterations of the program are required to find a converged solution; not only must the electron density converge as normal, so too must the atomic positions. If the atomic positions of the initial structure are sufficiently close to the DFT equilibrium positions, then geometry optimisation may not be required.

The key to successful modelling is therefore to run calculations at the lowest level of accuracy acceptable to the problem at hand. In order to facilitate this, preliminary testing of these key parameters for each material studied must be undertaken to identify their optimal values. Details of this testing for each system modelled in this thesis is described in the results (section 4.3) of Chapter 4.

2.2.4 Estimating exchange energies from DFT calculations

The Heisenberg model of a system with no anisotropy or external field, gives the total energy as,

$$E_{\text{tot}} = E_0 - 2 \sum_{\langle ij \rangle} S_i S_j J_{ij}, \quad (2.39)$$

where E_0 is the energy of the system excluding exchange interactions. Within the Heisenberg model, changes to the spin configuration of a material have no effect on the value of E_0 , which can be treated as a constant. By considering systems with many different spin configurations using spin-polarised DFT calculations, the exchange energies of magnetic materials can be estimated by mapping the total energies of these systems onto the Heisenberg model. The simplest example of this process is shown by a two atom system (Figure 2.6). The ferromagnetic configuration in (2.6a) gives the expression,

$$E_0 - 2JS^2 = E_{\text{fm}}, \quad (2.40)$$

where E_{fm} is the energy obtained through the corresponding DFT calculation of a ferromagnetic system. For the antiferromagnetic configuration (2.6b) the energy expression is given by,

$$E_0 + 2JS^2 = E_{\text{afm}}, \quad (2.41)$$

where E_{afm} is the energy obtained from an antiferromagnetic DFT calculation. An expression for J in terms of the DFT energies can be obtained by the elimination of E_0 from (2.40) and (2.41),

$$J = \frac{E_{\text{afm}} - E_{\text{fm}}}{4S^2}. \quad (2.42)$$

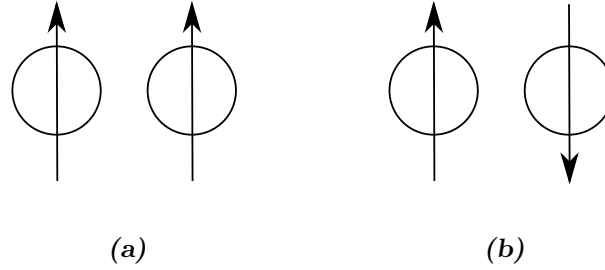


Figure 2.6: An example two atom system; (a) a ferromagnetic spin configuration, and (b) an antiferromagnetic spin configuration.

In the spinel based iron oxide/sulphide minerals of interest in this thesis there are three principal exchange energies to estimate. This necessitates four different spin configurations in order to obtain unique expressions for each value of J_{ij} . However, neither DFT or the Heisenberg model are exact descriptions of reality, and so using the minimum number of spin configurations may lead to poor results. In practice, the total energies of 10-20 different spin configurations are calculated to obtain an over-determined system of equations (Rocquefelte *et al.*, 2010; Nabi *et al.*, 2010). Least squares regression is then used to find the best fit values of J_{ij} (equation 2.39) for the range of spin configurations modelled.

2.3 Monte Carlo modelling

Monte Carlo (MC) methods are a class of numerical algorithms, which utilise random sampling in order to obtain results (*Landau and Binder, 2015*). They allow for the investigation of magnetic systems within the Heisenberg model without taking the mean-field approximation. MC methods are therefore able to simulate phenomena such as hysteresis, which makes them attractive to use for modelling the more general magnetic properties of systems. The Monte Carlo Metropolis algorithm (*Metropolis et al., 1953*) provides an approach to model temperature dependent equilibrium properties of systems. In magnetic systems this includes quantities such as magnetisation, susceptibility, energy and specific heat. It is an attractive method of modelling systems where the dynamical properties are not desired, due to its rapid convergence and ease of implementation (*Evans et al., 2014*). The thermodynamic basis for using the Metropolis algorithm is the assumption that all possible states of the system are accessible with an associated probability. The probability that such a state is occupied is given by the Boltzmann distribution, $\mathcal{P}_B$,

$$\mathcal{P}_B = \frac{\exp\left(-\frac{E(\alpha_i)}{k_B T}\right)}{Z}, \quad (2.43)$$

where $E(\alpha_j)$ is the energy of state α_i and Z is the partition function of the system. For a classical spin system the Metropolis algorithm (*Evans et al., 2014*) is as follows:

1. Choose a site i at random and rotate the spin $\mathbf{S}_i$ to a random trial position $\mathbf{S}'_i$.
2. Calculate the change in energy of the system, $\Delta E = E(\mathbf{S}_i) - E(\mathbf{S}'_i)$.
3. Evaluate the probability $P = \exp\left(-\frac{\Delta E}{k_B T}\right)$.
4. The trial move is then accepted if one of the following conditions is satisfied:
 - i. If $P > 1$ then accept the move, as this corresponds to a reduction of energy within the system.
 - ii. If $P \leq 1$, generate a random number $x = [0, 1]$. If $x < P$ then accept the move. Otherwise reject the move.

In a single Monte-Carlo step this process is repeated n times, where n is the number of spins in the system. All Monte Carlo algorithms must satisfy ergodicity, the requirement for all possible states of the system to be accessible, and reversibility, which requires that $P(\mathbf{S}_i \rightarrow \mathbf{S}'_i) = P(\mathbf{S}'_i \rightarrow \mathbf{S}_i)$. These are easy conditions to satisfy by merely choosing a trial direction at a random point of the unit sphere. A consequence of this approach is a low rate of move acceptance at low temperatures, where large deviations in the spin deviation are unlikely. Conversely, a trial move which has a high rate of acceptance is also problematic, as it makes it difficult for the system to stabilise into equilibrium.

Hinzke and Nowak (1999) developed an algorithm for choosing a trial spin which addresses these issues. By sampling a combination of trial moves, the algorithm is able to maintain a reasonable acceptance rate of trial moves across all temperatures (Figure 2.7). Three types of trial move are used; a spin flip, a cone move and a random move.

The spin flip is the equivalent of an Ising move where (*Evans et al.*, 2014),

$$\mathbf{S}'_i = -\mathbf{S}_i. \quad (2.44)$$

The cone move takes the initial spin direction and moves it to a new direction in the vicinity of the original spin according to the expression (*Evans et al.*, 2014),

$$\mathbf{S}'_i = |\mathbf{S}_i| \frac{\mathbf{S}_i + \sigma_g \mathbf{\Gamma}}{|\mathbf{S}_i + \sigma_g \mathbf{\Gamma}|} \quad (2.45)$$

where $\mathbf{\Gamma}$ is a random vector which is uniformly distributed over the surface of the unit sphere and σ_g is the width of the cone around the initial spin. The trial spin is first normalised and then multiplied by magnitude of the initial spin to preserve the length of the vector. $\mathbf{\Gamma}$ is chosen by the following algorithm:

1. Generate three random numbers in the range $[-0.5, 0.5]$ to correspond to x, y, z components of the vector $\mathbf{\Gamma}$.
2. If the length of the vector $\mathbf{\Gamma}$ is less than 0.5, then accept $\mathbf{\Gamma}$. This step ensures that the sampling is uniform within a sphere of radius 0.5.
3. Normalise $\mathbf{\Gamma}$ to ensure the sampling is now over the surface of the unit sphere.

σ_g is generally chosen to be of the form (*Evans et al.*, 2014),

$$\sigma_g = \frac{2}{25} \left(\frac{k_B T}{\mu_B} \right)^{1/5}. \quad (2.46)$$

The random move is chosen according to (*Evans et al.*, 2014),

$$\mathbf{S}'_i = |\mathbf{S}_i| \frac{\mathbf{\Gamma}}{|\mathbf{\Gamma}|}, \quad (2.47)$$

where the vector is again normalised and then multiplied by magnitude of the initial spin to preserve its length. The random move ensures that ergodicity is satisfied and allows all of the phase space to be efficiently sampled at high temperatures. At each trial step, one of the three moves is chosen at random. Spin distributions of the random move and Gaussian move are shown in Figure 2.8.

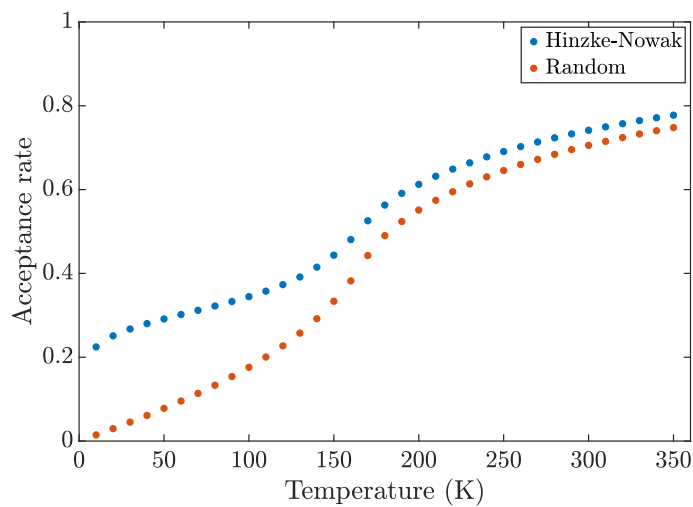


Figure 2.7: Acceptance rates of the Hinzke-Nowak algorithm and an algorithm only containing random moves. The system modelled is a $10 \times 10 \times 10$ simple cubic system with periodic boundary conditions. The temperature range runs through the Curie temperature, which occurs at ~ 170 K. Acceptance rates for the Hinzke-Nowak algorithm are higher at all temperatures, in particular at low temperatures.

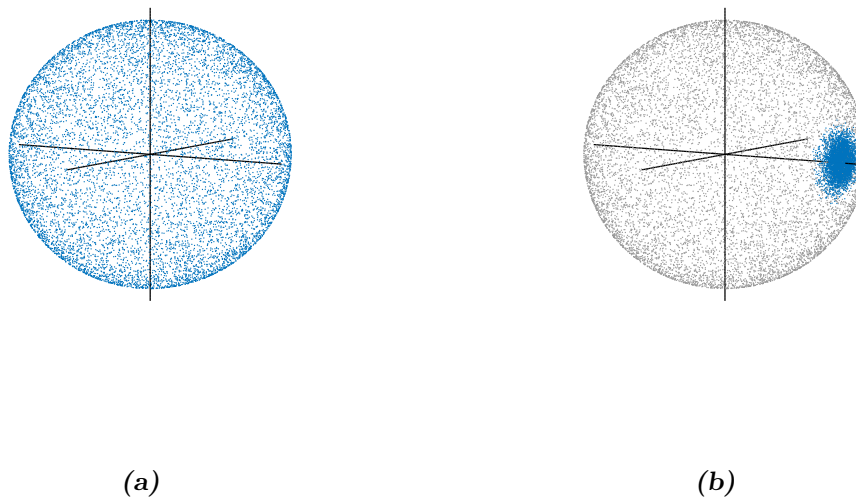


Figure 2.8: Spin distribution of different move types in the Hinzke-Nowak algorithm: (a) random moves and (b) Gaussian moves. The Gaussian moves are made from an initial spin aligned with the x-axis and can be seen clustered about the axis.

2.3.1 Calculating physical quantities within a Monte Carlo model

Monte Carlo methods start in an initial spin configuration and are iterated until they settle into equilibrium. There is no hard and fast rule for how long this process takes, but previous MC

models of similar type to the one described here typically use a period of 5,000-10,000 MC steps for the model to settle into thermal equilibrium. Due to the probabilistic nature of the MC technique, equilibrium is itself not a fixed state, with the precise spin configuration and energy of the system fluctuating as the system is iterated. This means that the value of physical quantities cannot be taken at a single point, and must instead be averaged over many MC steps.

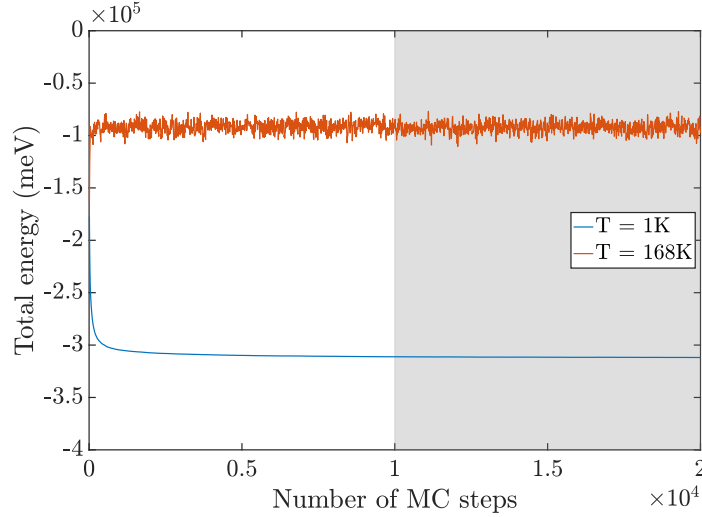


Figure 2.9: Total energy of a 10×10 simple cubic system over 20,000 MC steps. The case of $T = 1$ K was initialised in a random configuration of spins, and can be seen to settle into a low energy equilibrium state. The case of $T = 168$ K is close to T_C , and was initialised in an ordered state. The energy of the system rapidly increases, and settles into a higher energy equilibrium with larger fluctuations in energy than the low temperature case. The system is left to settle into equilibrium for the first 10,000 MC steps. Average values of the moments of energy and magnetisation are calculated over the second 10,000 MC steps.

The magnetisation of the system at any given point is given by,

$$M = \left| \sum_{i=1}^n \mathbf{S}_i \right|, \quad (2.48)$$

whilst the energy, E , is calculated from the system Hamiltonian. Magnetic susceptibility and specific heat are calculated from fluctuation relations by taking derivatives of the partition function, and are given by the expressions (*Newman and Barkema, 1999*),

$$\frac{\partial \langle M \rangle}{\partial H} = \chi = \frac{\langle M^2 \rangle - \langle M \rangle^2}{nT}, \quad (2.49)$$

and

$$\frac{\partial U}{\partial T} = c = \frac{\langle E^2 \rangle - \langle E \rangle^2}{nT^2}. \quad (2.50)$$

where U is the internal energy and n is the number of atoms in the system. Once the system has settled into equilibrium, the values of each moment E^k and M^k are recorded after each MC step. After a suitable number of MC steps have elapsed, the average values of each moment $\langle E^k \rangle$ and $\langle M^k \rangle$ can be calculated (Figure 2.9). Consultation of the literature suggests that averaging over at least 10,000 MC steps is commonplace (*Iglesias and Labarta, 2001; Mazo-Zuluaga et al., 2008; Evans et al., 2014*).

2.3.2 Testing and validation

A number of tests were conducted in order to ensure the correct implementation of the core components of the Monte Carlo model. The Boltzmann distribution for a single spin with uniaxial anisotropy can be used to test the implementation of the Monte Carlo integrator. The Boltzmann distribution for such a system is given by (*Evans et al., 2014*),

$$P(\theta) \propto \sin(\theta) \exp\left(\frac{-K_u \sin^2(\theta)}{k_B T}\right) \quad (2.51)$$

where θ is the angle from the easy axis. A system of 25×10^6 non-interacting spins ($J_{ij} = 0$) with uniaxial anisotropy was initialised in a random configuration and allowed to relax for 10,000 Monte-Carlo steps. The angle between each spin and the easy axis was recorded after relaxation. The resulting probability distributions for three values of $K_u/k_B T$ show very good agreement to the expected Boltzmann distribution from equation 2.51 (Figure 2.10) providing good evidence that the implementation of the Metropolis algorithm is correct.

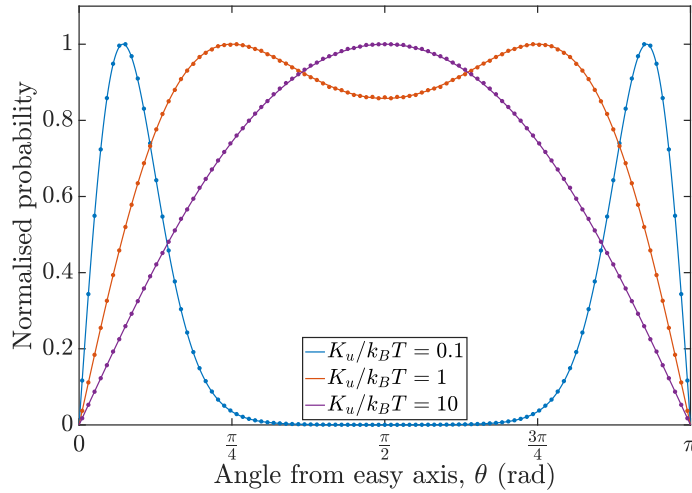


Figure 2.10: Calculated angular probability distribution for a system of 25×10^6 non-interacting spins with uniaxial anisotropy for three values of $K_u/k_B T$. The solid line donates the curve of equation 2.51. The distributions have been normalised to their maximum value.

Whilst the Boltzmann distribution gives a good test of systems of single or non-interacting

spins, no analytical solutions for systems of interacting spins exist. To this end, simulation results must be compared with the results obtained in previous Monte Carlo studies. A detailed investigation of the properties of the classical Heisenberg model using high-resolution MC techniques was undertaken by *Chen et al.* (1993). They obtained values for the inverse critical temperature,

$$K_C = \frac{J}{k_B T_C}, \quad (2.52)$$

of $K_C = 0.693$ for simple cubic systems and $K_C = 0.487$ for bcc systems in which $|\mathbf{S}_i| = 1$. The Hamiltonian used by *Chen et al.* (1993) was defined as,

$$\mathcal{H} = - \sum_{\langle ij \rangle} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j, \quad (2.53)$$

which is a factor of two smaller than the definition used in this model. Therefore we expect the Curie temperature of the MC model to be given by,

$$T_C = \frac{2J}{k_B K_C}. \quad (2.54)$$

In bulk magnetic systems T_C can be found from the peak susceptibility of a suitably large system, or by using Binder's U_4 cumulant (*Binder*, 1981),

$$U_4 = 1 - \frac{\langle M^4 \rangle}{3 \langle M^2 \rangle^2}. \quad (2.55)$$

The U_4 cumulant is calculated for a number of different system sizes and intersection of the cumulants as a function of temperature occurs at T_C .

Simple cubic and bcc systems were modelled using values of exchange energy of $J_{ij} = 5$ meV and $|\mathbf{S}_i| = 1$. T_C was estimated using both the maximum of susceptibility and Binder's U_4 cumulant in both cases. Values of $T_C = 167.4$ K for simple cubic and $T_C = 238.2$ K for bcc systems are expected from equation (2.54), which agree well with the results from the MC model (Figure 2.11).

2.3.3 Development of a classical spin Monte Carlo model

Magnetisation curves

When calculating magnetisation curves, a system is initialised in an ordered state. The simulation then runs through a set of temperatures between $T_{\min}$ and $T_{\max}$ in steps of ΔT . After each temperature has settled into equilibrium and average properties calculated, the temperature is iterated; the starting configuration of spins for each subsequent temperature is the final configuration of the previous temperature. Examples of the variation of magnetisation, susceptibility, energy and specific heat with temperature for a simple system are shown in Figure 2.12.

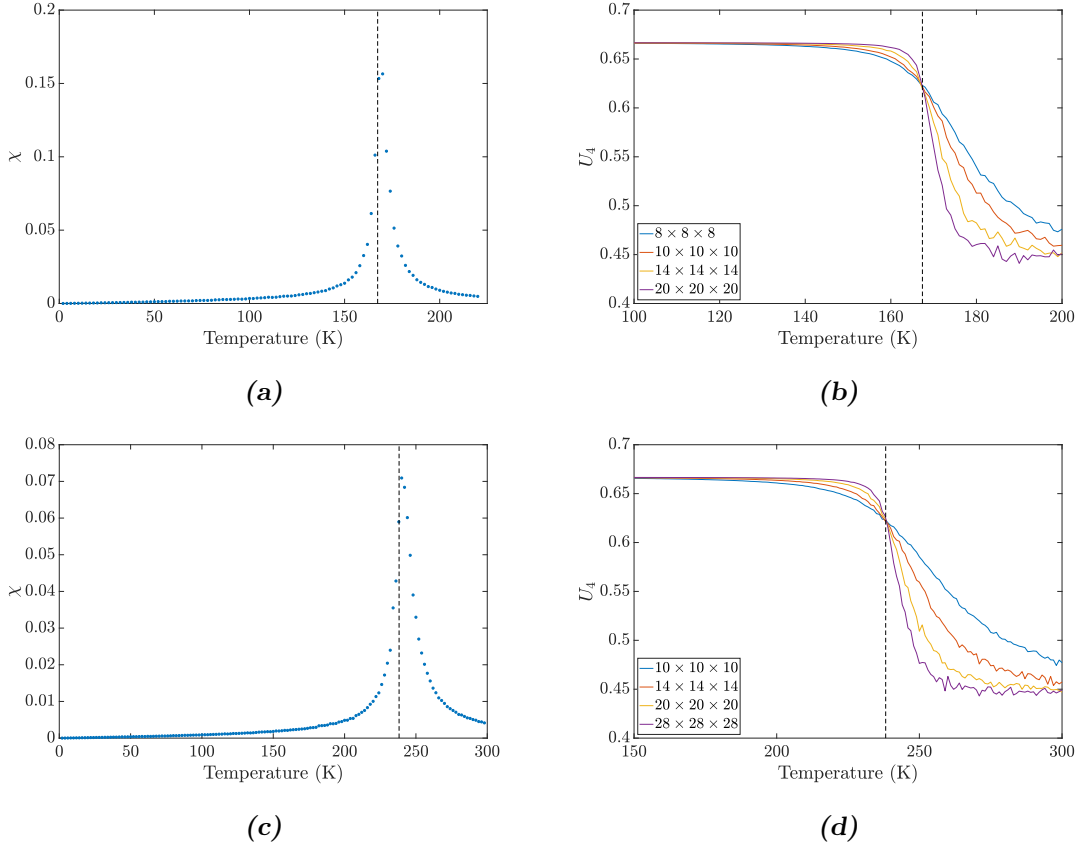


Figure 2.11: Comparison of T_C for sc (a-b) and bcc (c-d) systems to the values obtained from *Chen et al. (1993)*. (a) Susceptibility versus temperature of a $25 \times 25 \times 25$ sc system. (b) U_4 cumulant for sc systems of different lattice size. (c) Susceptibility versus temperature of a $28 \times 28 \times 28$ bcc system. (d) U_4 cumulant for bcc systems of different lattice size. The vertical dashed lines denote $T_C = 167.4$ K for simple cubic and $T_C = 238.2$ K for bcc systems as calculated from equation (2.54) using values of K_C from *Chen et al. (1993)*. The peaks in susceptibility and intersections of the U_4 cumulants both agree well with the value of T_C of *Chen et al. (1993)*.

Hysteresis loops

To simulate a hysteresis loop an external field is created to lie along a user defined direction, $\mathbf{H}$, with an initial magnitude $-H$. The system is initialised in a random configuration and allowed to settle into equilibrium at a high temperature $T > T_C$ and is then cooled down to the desired simulation temperature in user defined steps of ΔT . This ensures the system successfully aligns with the external field in equilibrium. To save computational time only one branch of the hysteresis loop is simulated, and the magnitude of the field is varied from $-H$ to H in steps of ΔH . The full hysteresis loop is then created by mirroring the result of the first branch to create the return branch. An example hysteresis loop is shown in Figure 2.13.

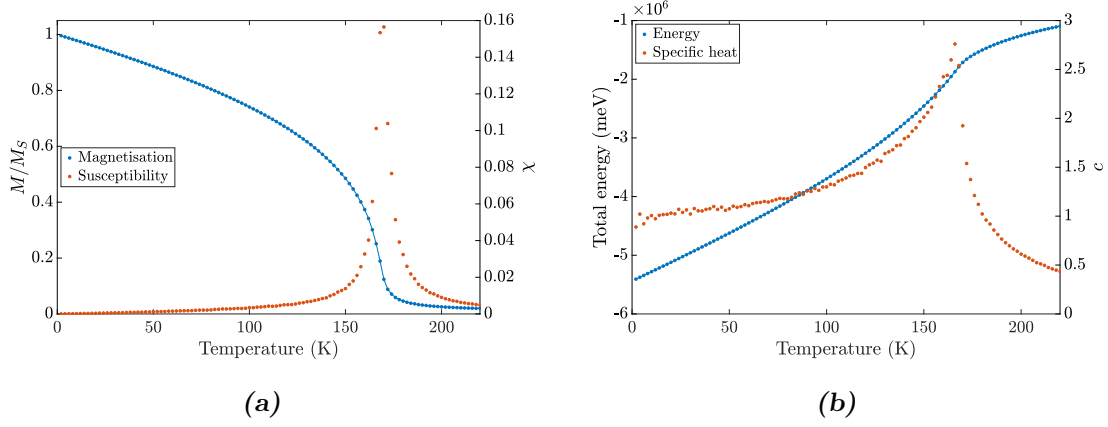


Figure 2.12: Example plots of (a) normalised magnetisation and susceptibility, and (b) total energy and specific heat against temperature for a $25 \times 25 \times 25$ simple cubic system with $|\mathbf{S}_i| = 1$, $J_{ij} = 5$ meV and periodic boundary conditions.

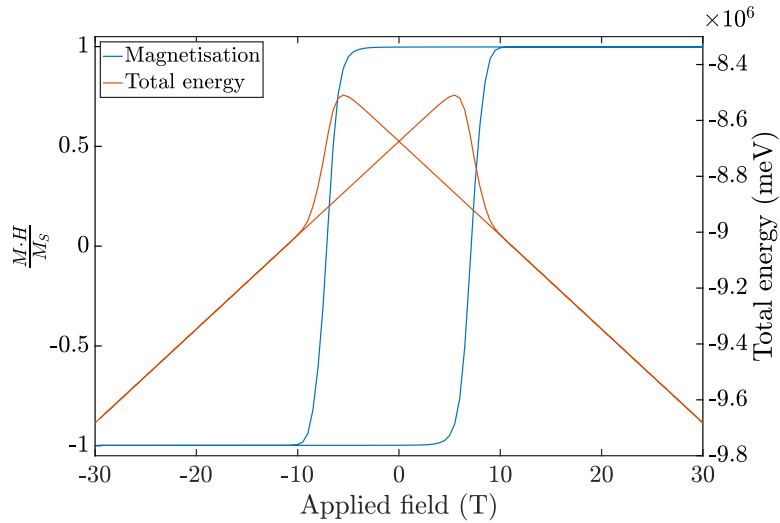


Figure 2.13: Example plot of normalised magnetisation and total energy against applied field. The test systems was a $10 \times 10 \times 10$ simple cubic system with $|\mathbf{S}_i| = 1$, $J_{ij} = 5$ meV, periodic boundary conditions and uniaxial anisotropy. The external field was aligned parallel to the easy axis.

Chapter 3

The effect of particle size and shape on the Curie temperature of magnetic nanoparticles

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3.1 Introduction

Interest in magnetic nanoparticles has grown rapidly over the past two decades across a wide range of scientific disciplines; applications in magnetic hyperthermia treatment (*Johannsen et al.*, 2010), improved contrast agents for MRI imaging (*Parkes et al.*, 2008) and heat-assisted magnetic recording (*Weller et al.*, 2013) are all actively being pursued. In the environment, magnetic nanoparticles have been proposed as the source of magnetic anomalies over oil fields (*Abubakar et al.*, 2015), and their presence in the human brain due to inhalation of anthropogenic pollution has recently been linked to Alzheimer's disease and other neurodegenerative diseases (*Maher et al.*, 2016). Despite this interest there are still several fundamental unanswered questions surrounding the magnetic behaviour of nanoparticles and other nanoscale structures. Many of these questions arise from a combination of interacting phenomena, making it no longer possible to simply use the bulk parameters to describe the magnetic nanoparticles' behaviour.

In bulk magnetic systems, the spin correlation length diverges at the Curie temperature, T_C , but in nanoscale systems the growth of the correlation length is limited by the smallest dimension of the system such that it causes a reduction in T_C . This obeys a finite-size scaling relationship (*Fisher and Ferdinand*, 1967),

$$\frac{T_C(\infty) - T_C(d)}{T_C(\infty)} = \left(\frac{d_0}{d}\right)^{\frac{1}{\nu}} \quad (3.1)$$

where $T_C(\infty)$ is the bulk Curie temperature, d_0 is a characteristic length scale of the system, ν is the correlation length scaling exponent and d is the smallest length scale of the system. Recent developments in preparation techniques have lead to several new experimental investigations of finite-sized scaling in magnetic nanoparticles. However, the results have been varied in contrast with the good agreement between theory and experiment found in studies of thin films (*Huang et al.*, 1993; *Ambrose and Chien*, 1996). Studies of hematite and magnetite nanoparticles have found values for ν in the range of 0.6 – 0.8 (*Li et al.*, 2014; *Wang et al.*, 2011b), close to the expected value of 0.7043 (*Chen et al.*, 1993) for the 3-D Heisenberg model. A value of $\nu = 1.06$ was determined from work conducted on Ni nanoparticles (*Wang et al.*, 2011a), with line dislocations near the surface of the nanoparticles suggested as the cause of this discrepancy.

Monte Carlo modelling of nano-scale systems has failed to clarify the situation, with values of ν derived from finite-size scaling also failing to agree with the accepted value of the correlation length scaling exponent. An Ising Monte Carlo simulation of maghemite nanoparticles suggested a value of $\nu = 0.49$ from finite-size scaling (*Iglesias and Labarta*, 2001), in clear disagreement with the 3-D Ising value of 0.6417 calculated from consideration of thermodynamic derivatives (*Ferrenberg and Landau*, 1991). Simulations of L1₀-FePt using a classical-spin Heisenberg model determined a value of $\nu = 1.06$ (*Lyberatos et al.*, 2012), again disagreeing with the generally accepted value. Long-range ordering was suggested as a possible source of this disagreement.

Here we use an atomistic mean-field model based on an approach previously used for analysing complex magnetic structures (*Fabian et al.*, 2015) and apply it to nanoscale systems. The model was applied to a number of crystal structures; simple synthetic systems with uniform spin and exchange energies, and a model of magnetite (Fe₃O₄). The effect of shape on the Curie temperature of magnetic nanoparticles was studied and finite-size scaling in these systems considered.

3.2 Mean-field modelling of magnetic nanoparticles

The mean-field approximation is a well understood method for analysing the behaviour of magnetic systems, having been successfully applied across the spectrum of magnetic models from the Ising model to spin glasses (*Mezard et al.*, 1987; *Christensen and Moloney*, 2005). The generalised mean-field equations for a system of interacting Heisenberg spins are given by,

$$m_i = B_{S_i} \left(S_i \frac{\sum_{j \in N_i} 2J_{ij} S_j m_j + g\mu_B h}{k_B T} \right), \quad (3.2)$$

where m_i is the normalised magnetisation of site i , S_i is the spin at site i , B_{S_i} is the Brillouin function, J_{ij} is the isotropic exchange interaction between sites i and j defined such that ferro-magnetic exchange is positive, $g \approx 2$ is the gyromagnetic ratio, μ_B is the Bohr magneton, h is an

external magnetic field acting on each site, k_B is the Boltzmann constant, and T is temperature. The sum over j acts over the set of nearest neighbours of i , where $N_i := \{j : J_{ij} \neq 0\}$. Each site i is a spin in the system being studied, and so can represent the unique atoms in a complex crystal lattice (Fabian *et al.*, 2015), the layers in a thin film (Jensen *et al.*, 1992), or as in the case being studied here, the atoms in a magnetic nanoparticle. A full derivation of the mean-field equations is given in Appendix A.

The mean-field equations in the form of (3.2) are a system of N coupled non-linear equations. Because its solution is not analytically tractable, a numerical approach must be taken. By recasting (3.2) as,

$$f_i = B_{S_i} \left(S_i \frac{\sum_{j \in N_i} 2J_{ij} S_j m_j + g\mu_B h}{k_B T} \right) - m_i = 0, \quad (3.3)$$

the problem is transformed to finding a common zero of the set of expressions f_i . There is normally more than a single solution to such systems of equations, and so further conditions must be fulfilled by the desired solution. In the case of the mean-field equations, the trivial root $m_i = 0$ is not a valid solution below T_C , when it falls at a maximum of free energy. In addition, m_i are normalised magnetic moments, they all must lie in the range $-1 \leq m_i \leq 1$.

The system of equations described by (3.3) was solved by a C++ program using the SNES solvers of the Portable, Extensible Toolkit for Scientific Computation (PETSc) libraries (Balay *et al.*, 2016). PETSc uses N -dimensional Newton based methods that require either an analytic expression or a finite-difference approximation of the Jacobian $\left(\frac{\partial f_i}{\partial m_j}\right)$ to iteratively solve systems of non-linear equations. In the case of (3.3), an analytic expression for the Jacobian can be obtained. For $i = j$,

$$\frac{\partial f_i}{\partial m_i} = -1. \quad (3.4)$$

For $j \in N_i$,

$$\frac{\partial f_i}{\partial m_j} = \frac{2J_{ij} S_j}{k_B T} \left[\left(\frac{1}{2S_i} \right)^2 \frac{1}{\sinh^2 \left(\frac{1}{2S_i} \xi_i \right)} - \left(\frac{2S_i + 1}{2S_i} \right)^2 \frac{1}{\sinh^2 \left(\frac{2S_i + 1}{2S_i} \xi_i \right)} \right], \quad (3.5)$$

where,

$$\xi_i = \frac{\sum_{j \in N_i} 2J_{ij} \langle S_j \rangle + g\mu_B h}{k_B T}. \quad (3.6)$$

Otherwise for $i \neq j$ and $j \notin N_i$,

$$\frac{\partial f_i}{\partial m_j} = 0. \quad (3.7)$$

3.2.1 Crystal structures and particle shapes

Particles were modelled using simple cubic, body-centered cubic and inverse spinel (magnetite) crystal structures. For each crystal structure, five different shapes were studied: cubes, spheres, and three elongated needle-like shapes with aspect ratios of 2:1:1, 5:1:1 and 10:1:1. Each shape was modelled over a range of sizes (see Table 3.1). Spherical particles were approximated on the crystal lattice by including an atom if it lay within $\frac{d}{2}$ of the centre of the particle.

Table 3.1: Range of smallest length scales, d , for all particles modelled in terms of number of atoms. Not all particle diameters in the range were calculated. For spinel systems, particle sizes are also listed in nm for the case of magnetite.

		Cube	Sphere	Needle		
				2:1:1	5:1:1	10:1:1
Simple cubic		2–45	3–50	2–40	2–24	2–19
Bcc		3–67	5–67	3–41	3–37	3–29
Spinel	(atoms)	8–104	8–120	8–76	8–56	8–44
	(nm)	0.84–10.92	0.84–12.60	0.84–7.98	0.84–5.88	0.84–4.62

Simple cubic (sc) and body-centred cubic (bcc) particles were modelled with an isotropic spin of $S=2$ applied to each atom, and a ferromagnetic exchange energy of $J = 3.5 k_B \approx 0.3$ meV between each nearest neighbour.

We also considered magnetite (Fe_3O_4), as it is an important and well understood natural mineral, which forms in the inverse spinel structure (Figure 1.8). 32 oxygen (O^{2-}) atoms form a face centered cubic lattice, with 24 iron atoms occupying tetrahedral (A) and octahedral (B) interstitial sites. 8 Fe^{3+} atoms occupy the A sites, whilst the 16 B sites are occupied by an equal number of randomly distributed Fe^{3+} and Fe^{2+} ions (*Shull et al.*, 1951). The magnetic structure of magnetite is ferrimagnetic, with the magnetic moments of the A and B sites aligned in opposing directions. The total theoretical moment of magnetite is $4\mu_B$ per formula weight, in close agreement with the experimentally determined value of $4.1\mu_B$ (*Dunlop and Özdemir*, 1997).

For the model of magnetite, spins of $S_A = 2.5$ and $S_B = 2.25$ were assigned to the A and B sites. Nearest-neighbour exchange energies of $J_{AA} = -1.56$ meV $J_{AB} = -2.38$ meV $J_{BB} = 0.26$ meV were used as the most complete set of experimental estimations (*Bourdonnay et al.*, 1971).

3.2.2 Determining the Curie temperature

Previous studies determined the Curie temperature by linearising the Brillouin function in equation (3.2), and then solving the arising matrix equation for the case of a singular matrix (*Fabian et al.*, 2015). This approach rapidly became too expensive here given the large number of unique sites even in small particles, and so an alternative approach was used.

The solution of the mean-field equations gives the magnetisation of each atom in the particle for a given temperature, T . Below T_C , this gives a non-zero value of magnetisation for each site; for $T \geq T_C$, magnetisation at each site is zero. It is therefore possible to determine T_C by a bisection algorithm. Two initial temperatures were chosen, $T_L = 1$ K and $T_H > T_C(\infty)$. The magnitude of the average magnetisation of the particle, $|\langle m_i \rangle|$, at the midpoint between these two temperatures,

$$T_M = \frac{T_L + T_H}{2}, \quad (3.8)$$

was calculated. If at this temperature $|\langle m_i \rangle|$ was found to be greater than a threshold value $\epsilon_m = 0.0001$, then T_M was assumed to be below the Curie temperature, and T_L was replaced by T_M . For $|\langle m_i \rangle| < \epsilon_m$, T_H was replaced by T_M . This process was iterated, until $T_H - T_L < 0.01$ K. The Curie temperature of the particle was then taken as,

$$T_C = \frac{T_{L_f} + T_{H_f}}{2}, \quad (3.9)$$

where T_{L_f} and T_{H_f} are the final values of T_L and T_H respectively and the error in T_C is,

$$\epsilon_{\text{err}} = \frac{T_{L_f} - T_{H_f}}{2}. \quad (3.10)$$

Excellent agreement in the value of T_C between the two methods, typically better than 0.02 K, was found in small simple cubic systems.

3.3 Results and Discussion

3.3.1 Properties of nanoparticles

Normalised magnetisation curves, $m(T)$, were calculated in steps of $\Delta T = 0.1$ K for bcc and sc particles, and $\Delta T = 1$ K for magnetite particles. A sharp Curie-temperature phase transition can be seen for all particles, with the Curie temperature decreasing with decreasing particle size (Figure 3.1). In real systems of this size, identifying the Curie temperature is more complex; the superparamagnetic nature of many magnetic nanoparticles requires measurements to be made in the presence of an external field, which destroys the second-order phase transition, whilst samples will inevitably contain a distribution of grain sizes and morphologies (*Fabian et al.*, 2013).

The very smallest bcc (not shown) and the magnetite particles have more ‘linear’ m-T curves than larger particles of the same crystal structure. Their behaviour is strongly influenced by atoms in the corners of the cubes, which have only one or two nearest neighbours. The bulk Curie temperature of magnetite was calculated as $T_C(\infty) = 1108$ K using the mean-field model, which is ~ 250 K higher than the experimental value of 850 K (*Dunlop and Özdemir*, 1997). A higher Curie temperature than the experimental result is frequently found by the mean-field approach.

This discrepancy arises from the importance of fluctuation correlations in real systems, which have the effect of reducing the Curie temperature.

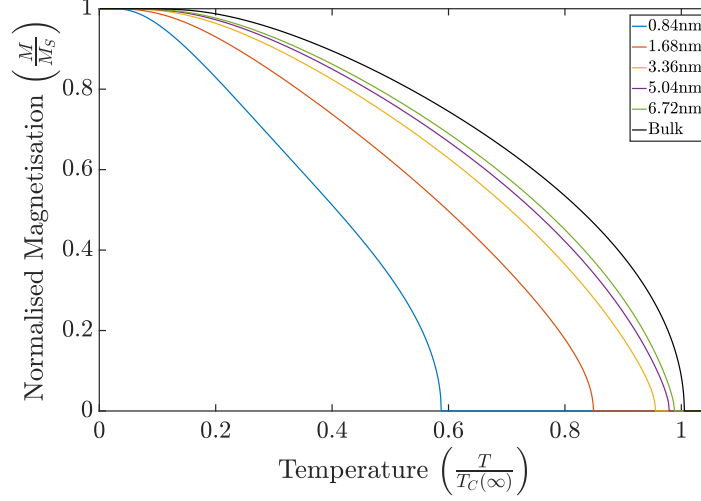


Figure 3.1: Magnetisation curves against normalised temperature of cubic magnetite particles of a number of different sizes. The bulk mean-field magnetisation curve is included for reference, where $T_C(\infty) = 1108$ K in the mean-field model. Particle sizes are given in nm.

Magnetisation varies spatially throughout the nanoparticles at all temperatures (Figure 3.2). At low temperatures, a core-shell like structure is seen, in which a core of atoms behave in a bulk-like manner, surrounded by a shell of atoms exhibiting reduced magnetisation. As the temperature increases, this boundary softens, and there is a more gradual change in magnetisation throughout the particle. This behaviour has previously been observed (*Shcherbakov et al.*, 2012).

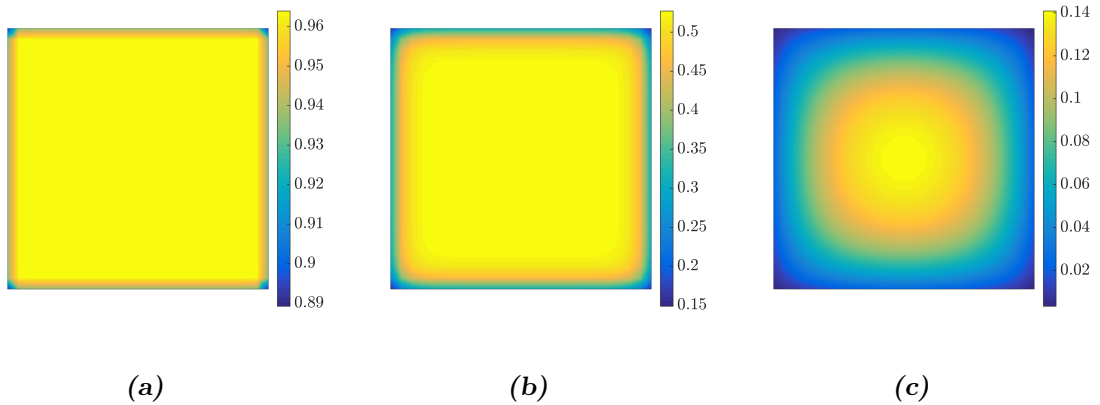


Figure 3.2: Variation of magnetisation in a cube of $25 \times 25 \times 25$ atoms arranged in a simple cubic lattice. A slice through the middle of the particle at $z = 13$ is shown at three different normalized temperatures: (a) $t = 0.36$ (b) $t = 0.87$ (c) $t = 0.99$, where $t = \frac{T}{T_C(d)}$.

3.3.2 Effect of varying particle shape

The Curie temperature of small magnetic nanoparticles is affected by the shape of the particle (Figure 3.3). Spherical particles have the lowest Curie temperature for a given size, d , with cubic, 2:1:1, 5:1:1 and 10:1:1 particles having successively higher values of T_C .

Whilst plotting T_C against the shortest length of a particle is the standard method of investigating the change in T_C due to size in the literature, this approach does neglect the large volume differences between particles of different shapes which are considered the same size by that method. For example, the number of atoms in a 10:1:1 particle of size d , is an order of magnitude higher than a spherical or cubic particle of the same size, d . To investigate this further, T_C was plotted against the cube root of the volume of the particle (Figure 3.4). This plots the Curie temperature against an effective particle size equivalent to that of a cube with the same volume. Using this method of analysis, spheres have the highest Curie temperature with cubes, 2:1:1, 5:1:1 and 10:1:1 particles having successively lower Curie temperatures. This is due to the more compact shape of a sphere, which leads to both fewer atoms on the surface and a greater average distance from the surface for atoms inside the sphere.

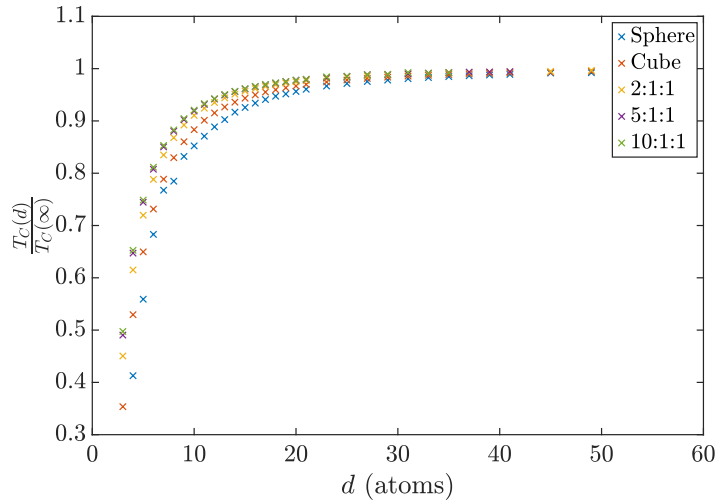


Figure 3.3: Normalised Curie temperature of bcc nanoparticles. Data for five shapes is shown; spherical, cubic, 2:1:1, 5:1:1 and 10:1:1 particles.

The normalised difference in the Curie temperature between spherical and 10:1:1 particles is defined as,

$$\Delta T_C(d) = \frac{T_{C_{10:1:1}}(d) - T_{C_{\text{sph}}}(d)}{T_C(\infty)}, \quad (3.11)$$

and is used as a measure of the strength of the influence of shape on T_C . In the smallest particles, ΔT_C is found to be 15-25 % of $T_C(\infty)$ before it falls off rapidly as particle size increases (Figure 3.5a). The size at which ΔT_C become negligible (taken as $\Delta T_C < 0.02$) varies between crystal

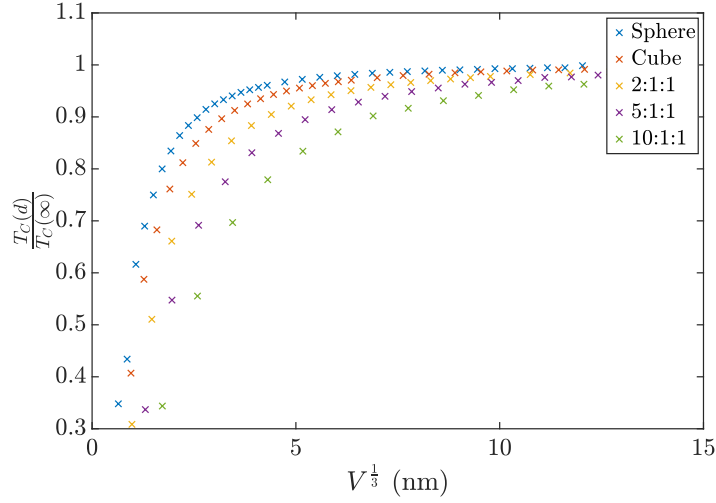


Figure 3.4: Normalised Curie temperature against the cube root of the volume for magnetite nanoparticles. Data for five shapes is shown; spherical, cubic, 2:1:1, 5:1:1 and 10:1:1 particles.

structures. In simple cubic and bcc particles this occurs at a size of 10 and 20 atoms respectively. For magnetite, our results suggest that shape is only an important factor in particles smaller than 5 nm (≈ 50 atoms) in size.

The sensitivity of ΔT_C with respect to the relative magnitudes of exchange energy was tested in magnetite (Figure 3.5b). Two additional sets of calculations were made, one using estimations of exchange energies from *ab initio* calculations (Uhl and Siberchicot, 1995), and another using uniform values of $J = 3.5k_B$. The latter choice creates an artificial ferromagnetic system, with the value of J selected to match the other systems modelled in this work. For all particle sizes, except for the smallest size $d = 0.8$ nm, the value of ΔT_C does not change appreciably as exchange energies differ. When $d = 0.8$ nm, a small difference in the value of ΔT_C of 0.05 was seen between the ferromagnetic and two ferrimagnetic systems. This suggests that the relative magnitudes of exchange energies have little bearing on the value of ΔT_C , and that the size below which shape begins to have an impact on the Curie temperature is controlled predominantly by crystal structure.

Whilst ΔT_C cannot be directly computed when investigating the effect of shape using the cube root of the volume, Figure 3.4 shows that the difference in Curie temperature between magnetite particles of different shapes is enhanced when considering shape in this way in comparison to using the smallest particle dimension. When using the cube root of the volume as a measure of particle size, the difference in Curie temperature due to shape is still large at 5 nm, $\sim 20\%$ of the bulk value of T_C , and does not become negligible until particles have a equivalent size of approximately 12 nm. This difference in results between the two methods also highlights the importance of using directly comparable methods for calculating the particle size of samples, in particular when comparing the results of different studies.

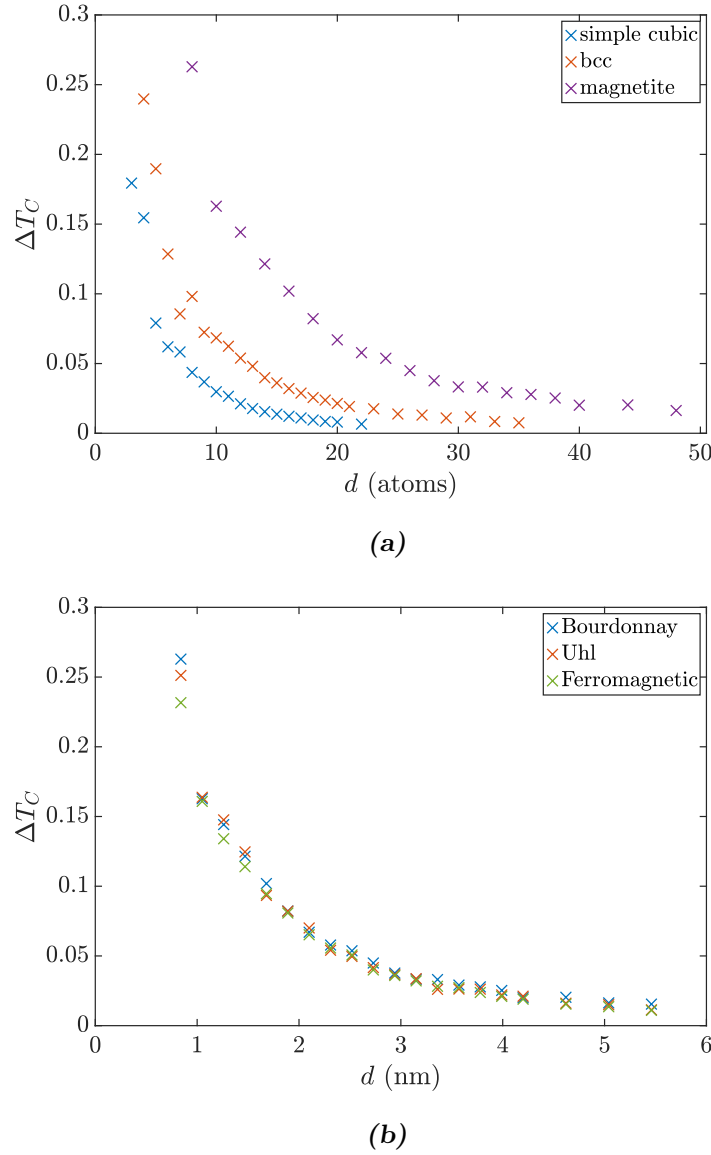


Figure 3.5: ΔT_C as a function of d . (a) Illustrates the effect of variation due to crystal structure. (b) Illustrates the effect of changes to exchange energy in magnetite between experiment (Bourdonnay et al., 1971), *ab initio* modelling (Uhl and Siberchicot, 1995) and an artificial ferromagnetic system.

3.3.3 Finite-size scaling

Values for the scaling exponent ν were calculated by non-linear least squares regression to equation (3.1) using the Levenberg-Marquardt algorithm (Levenberg, 1944). The error in ν was taken as the 95% confidence interval of the best fit value. Particles of different materials and shapes were considered separately. Fitting was undertaken initially on all sizes of particles from a particular system, and then successively removing the smallest particle from the fit. The final value of ν was taken as the one with the smallest error, in order to account for any deviation from scaling

behaviour seen at small sizes.

The chosen fits describe much of the data well, with deviation away from scaling behaviour for diameters smaller than $d \approx 10$ atoms for simple cubic systems, $d \approx 15$ atoms for bcc systems and $d \approx 20$ atoms for magnetite systems (examples of fitting shown in Figure 3.6). Values of ν are close to the analytical mean-field result of $\nu = 0.5$ (Stanley, 1987) in all cases, lying in the range 0.46-0.55 (Figure 3.7). No trend in the value of the scaling exponent with respect to particle shape can be seen. This consistency of results close to the accepted value of the scaling exponent contrasts with the range of values of ν found in other studies (Li *et al.*, 2014; Wang *et al.*, 2011b,a; Lyberatos *et al.*, 2012).

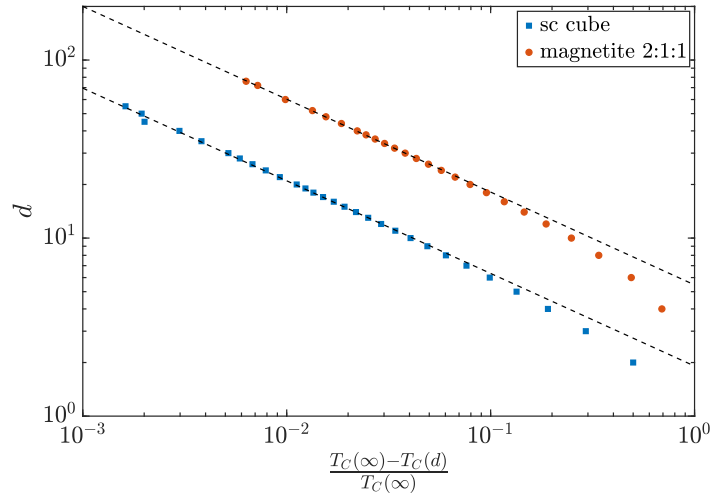


Figure 3.6: Example fits to determine the value of the scaling exponent ν for cubic sc and magnetite 2:1:1 particles. The dashed lines show the best fits to equation (3.1) where the error in ν is minimised.

An analytical expression for the Curie temperature of some types of nanoparticle has been derived from Ginzberg-Landau (G-L) theory (Shcherbakov *et al.*, 2012). This approach has been applied to cubic and long needle particles of simple cubic, body centred cubic and face centred cubic structure. A modified scaling law is predicted in which,

$$\frac{T_C(\infty) - T_C(d)}{T_C(\infty)} = \kappa \left(\frac{\pi}{d+2} \right)^2, \quad (3.12)$$

where κ depends upon the shape and crystal structure of the particle. For a simple cubic structure, $\kappa = \frac{1}{2}$ for a cubic particle and $\kappa = \frac{1}{3}$ for a long needle. For a body centred cubic structure, $\kappa = \frac{3}{2}$ for a cubic particle and $\kappa = 1$ for a long needle.

The difference in Curie temperature between 5:1:1 and 10:1:1 particles in the mean-field model is very small (Figure 3.3), suggesting that the 10:1:1 particle is a good approximation to a long needle. We can therefore directly compare the analytical result above with the results from the

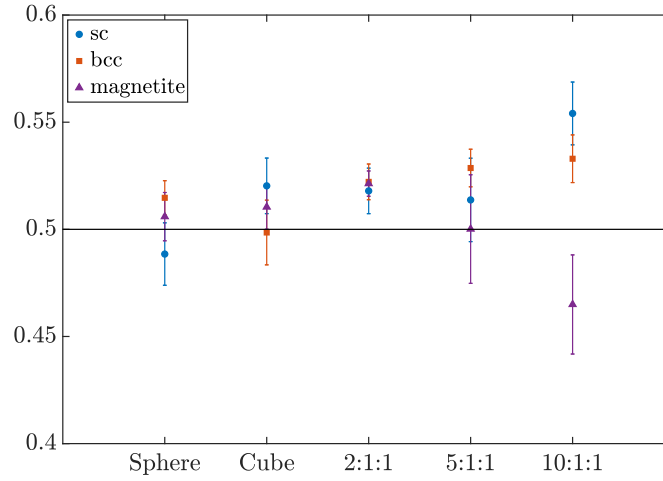


Figure 3.7: Calculated values of ν for simple cubic, bcc and magnetite systems. Errors donate 95% confidence interval of the fit. Solid line highlights the analytical mean-field value of $\nu = 0.5$.

mean-field model. The G-L theory clearly captures the deviation away from finite-size scaling seen in the mean-field approach at very small length scales (Figure 3.8). However, the quantitative agreement between the two models varies. For cubic bcc particles, the two models agree very closely, but for simple cubic 10:1:1 particles a larger difference in predictions can be seen; G-L theory predicts a value of T_C approximately half of the value of mean-field theory for the smallest systems.

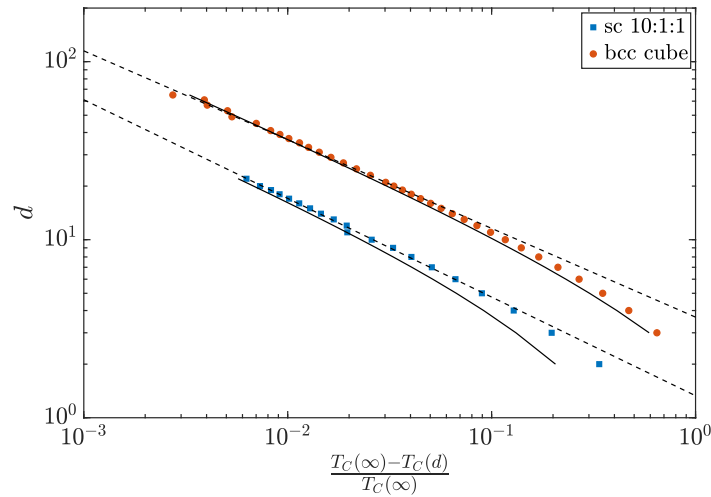


Figure 3.8: Comparison of the finite-size scaling law (3.1), and the modified scaling law (3.12) in cubic bcc and simple cubic 10:1:1 particles. The solid lines show the analytical results from (3.12). The dashed lines show the best fit to equation (3.1) where the error in ν is minimised.

The qualitative accuracy of the modified scaling law was tested by fitting the mean-field data

to a law of the general form of (3.12),

$$\frac{T_C(\infty) - T_C(d)}{T_C(\infty)} = \left(\frac{d_0}{d+2} \right)^{\frac{1}{\nu}}. \quad (3.13)$$

In contrast to the fitting procedure for finding ν used earlier, only a single fit of all data points was made in order to test (3.13) across all length scales. The results for simple cubic and bcc particles show that the general form of the modified law describes the scaling behaviour at small length scales well (Figure 3.9). However, for magnetite particles, equation (3.13) does not describe the scaling behaviour at small length scales, with deviation away from this law clearly seen. We suggest this is due to the complex crystal structure of magnetite which involves interactions over many layers of the unit cell. This is in contrast to the simpler sc, bcc and fcc ordering, which only interact with neighbours in adjacent layers, for which equation (3.12) is derived.

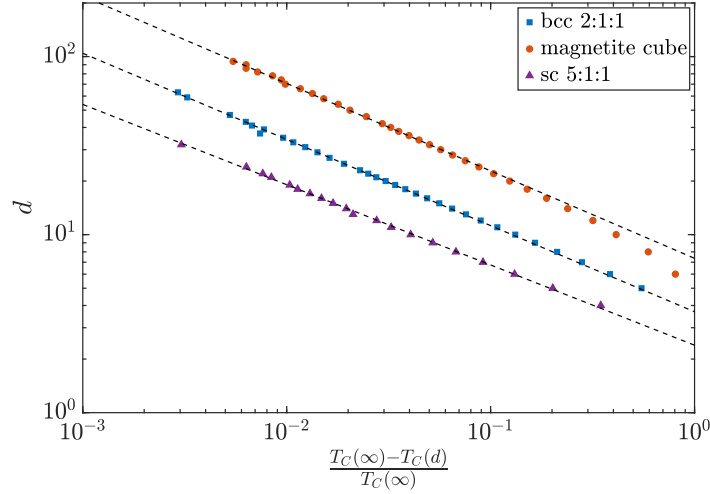


Figure 3.9: Example fits to the general modified scaling law (3.13) for bcc 2:1:1, cubic magnetite and sc 5:1:1 particles. The dashed lines show the best fits to equation (3.13) where all particles are included in the fit.

3.3.4 Coordination number

In the bulk mean-field Heisenberg model the Curie temperature, $T_C(\infty)$, is described to a good linear approximation by,

$$T_C(\infty) = \frac{(S+1)}{3S} \frac{2zJS^2}{k_B}, \quad (3.14)$$

where S is the isotropic spin, z is the number of nearest neighbours and J is the isotropic exchange energy. In the bulk case, the Curie temperature is linearly dependent on the number of nearest neighbours in the system, assuming all other variables are held constant. In view of the relationship

between T_C and z in (3.14), it may seem reasonable to assume that $T_C(d)$ can be described to a good approximation by the average coordination number $\langle z \rangle$,

$$T_C(d) = \frac{(S+1)}{3S} \frac{2\langle z \rangle JS^2}{k_B}. \quad (3.15)$$

By considering the left hand side of the scaling equation (3.1), and substituting in equations (3.14) and (3.15) an expression for scaling as a function of average coordination number is then obtained,

$$t = \frac{T_C(\infty) - T_C(d)}{T_C(\infty)} = 1 - \frac{\langle z \rangle}{z}. \quad (3.16)$$

Analytic expressions for $\langle z \rangle$ in cubic sc and bcc particles can be found and are given by,

$$\langle z_{sc} \rangle = 6 - \frac{6}{d}, \quad (3.17)$$

and

$$\langle z_{bcc} \rangle = \frac{4(2d^3 - 6d^2 + 6d + 8)}{d(d^2 + 3)}. \quad (3.18)$$

By further substituting in the expressions for $\langle z_{sc} \rangle$ and $\langle z_{bcc} \rangle$ into (3.16) expressions for t_{sc} and t_{bcc} in terms of d are obtained. For a simple cubic system, where $z = 6$,

$$\frac{T_C(\infty) - T_C(d)}{T_C(\infty)} = 1 - \left(\frac{6 - \frac{6}{d}}{6} \right) = \frac{1}{d}, \quad (3.19)$$

which is a powerlaw of the form in equation (3.1) where $\nu = 1$ and $d_0 = 1$. For a bcc system, where $z = 8$,

$$\frac{T_C(\infty) - T_C(d)}{T_C(\infty)} = 1 - \frac{\left(2 - \frac{6}{d} + \frac{6}{d^2} + \frac{8}{d^3} \right)}{2 + \frac{6}{d^2}}. \quad (3.20)$$

The d^{-2} and d^{-3} terms quickly become small compared to the d^{-1} term, and so,

$$\frac{T_C(\infty) - T_C(d)}{T_C(\infty)} \rightarrow 1 - \left(\frac{2 - \frac{6}{d}}{2} \right) = \frac{3}{d}, \quad (3.21)$$

which again recovers a powerlaw where $\nu = 1$ (and $d_0 = 3$). This result is in clear contrast to the mean-field value of $\nu = 0.5$ and shows that the assumption made in (3.15) does not hold in the mean-field approximation (also shown in Figure 3.10). A previous study of magnetic nanoparticles using the free-energy variational principle found that the expression in (3.16) was true to a first approximation in that model (Velásquez *et al.*, 2011). The value for the scaling exponent obtained by the variational method for both bcc and fcc lattices was found to be $\nu = 1.0001 \pm 0.0001$, in agreement with the result obtained above.

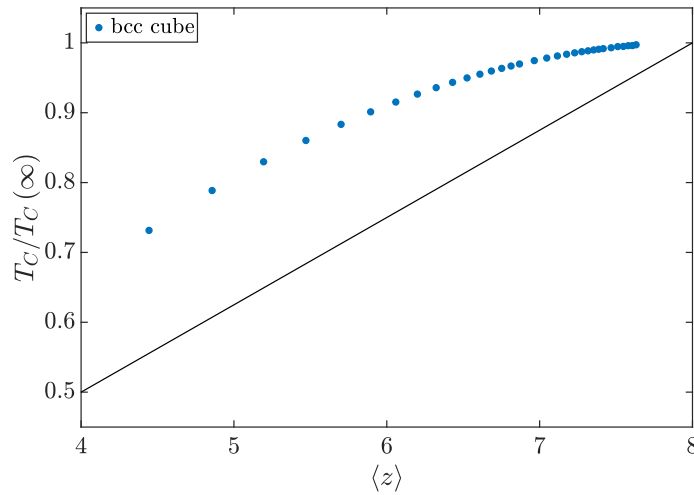


Figure 3.10: Plot of reduced Curie temperature against average coordination number for bcc nanoparticles. The solid line shows the linear relationship suggested in (3.15). No agreement between this relationship and the numerical results can be seen.

3.4 Conclusions

This study has used the mean-field approximation applied to finite systems of Heisenberg spins to investigate the particle size and shape dependence of the Curie temperature of magnetic nanoparticles. A numerical model was developed to solve the generalised mean-field equations for a number of particle shapes and crystal structures.

T_C was found to vary between different shapes of particle, with spheres, cubes, 2:1:1, 5:1:1 and 10:1:1 particles having successively higher values of Curie temperature for the same smallest dimension. ΔT_C , the difference in Curie temperature between 10:1:1 and spherical particles, was found to be 15-25% of the value of $T_C(\infty)$ in particles a few atoms across and rapidly decreased as particle size increased. The size at which ΔT_C became negligible was found to differ between crystal structures. For magnetite this was found to be 5nm. ΔT_C was also found to be insensitive to changes in the exchange energy between neighbouring atoms, showing that crystal structure is the primary driver of the differences in T_C due to shape.

All systems were fit to the finite-size scaling law and a good fit was found in all cases. Very small particles, typically $d < 10$ -20 atoms, showed deviation away from finite-size scaling behaviour. Values of ν were found to lie in the range 0.46-0.55, which compare well to the analytical mean-field value of 0.5. No trend in the value of ν with relation to particle shape was found. A modified scaling law, derived from Ginzberg-Landau theory, accounted for the observed deviation from finite-size scaling in simple cubic and bcc particles, but was not successful when applied to magnetite.

Chapter 4

Estimation of magnetic exchange energies in magnetite and maghemite

4.1 Introduction

In order to model partially oxidised magnetite nanoparticles with Monte Carlo techniques, estimates of the three principal exchange energies J_{AB} , J_{AA} and J_{BB} are required. As discussed in section 1.4.1, exchange energies in magnetite have previously been estimated using a variety of experimental and *ab initio* techniques (e.g *Brockhouse and Watanabe*, 1963; *Bourdonnay et al.*, 1971; *Uhl and Siberchicot*, 1995). To my knowledge, estimates of exchange energies in maghemite have never been made, either numerically or experimentally.

Previous studies have shown that estimates of J_{ij} in transition metal oxides using DFT can be made using the least-squares method described in section 2.2.4 (*Nabi et al.*, 2010; *Rocquefelte et al.*, 2010). Different techniques for estimating J_{ij} require different approximations, and so it is desirable that the exchange energies used in the Monte Carlo model are estimated using a consistent framework. In this Chapter, the Wien2k DFT code is used to estimate J_{AB} , J_{AA} and J_{BB} in magnetite and maghemite using the least-squares method.

In section 4.3.1 spin polarised GGA+U calculations are performed on magnetite to: (1) ensure that all estimates of J_{ij} were made in a consistent framework, and (2) test the least-squares method on a spinel iron oxide with a simpler crystal structure. Results of these calculations are discussed and compared to previous work. In section 4.3.2 the same method was applied to the more complex structure of maghemite; however the presence of vacancies within the crystal structure led to irresolvable difficulties in estimating J_{ij} . Details of the calculations and techniques used to try and obtain results are discussed.

4.2 Formulation of spin configurations

The least-squares method requires the creation of n magnetic spin configurations which gives rise through equation (2.39) to a system of n equations which can be written in matrix form as,

$$\begin{bmatrix} A_{11} & A_{12} & \cdots & A_{1m} \\ A_{21} & A_{22} & \cdots & A_{2m} \\ \vdots & \vdots & \ddots & \vdots \\ A_{n1} & A_{n2} & \cdots & A_{nm} \end{bmatrix} \begin{bmatrix} J_1 \\ J_2 \\ \vdots \\ J_m \end{bmatrix} = \begin{bmatrix} E_1 - E_0 \\ E_2 - E_0 \\ \vdots \\ E_n - E_0 \end{bmatrix} \quad (4.1)$$

where $\mathbf{A}$ is the matrix of coefficients, $\mathbf{J}$ the vector of exchange energies to be found and E_n is the total exchange energy of the n^{th} spin configuration. In principle this technique allows for any number of J_{ij} values to be estimated, provided that enough spin configurations are modelled to ensure an over determined system of equations. However, as more exchange energies are added into the model the increasing number of parameters may mean that a range of different parameter values give similarly good mathematical fits to the data. As an example of this, *Blukis* (2018) was able to obtain better mathematical fits to Monte Carlo chemical interaction parameters in Ni-Fe structures using random parameter values than was achieved in other published work using the least squares method. To minimise the probability of this effect occurring, fitting is restricted in this work to the nearest neighbour exchange energies, J_{AB} , J_{AA} and J_{BB} . The matrix equation (4.2) is therefore reduced to,

$$\begin{bmatrix} A_{1(AB)} & A_{1(AA)} & A_{1(BB)} \\ \vdots & \vdots & \vdots \\ A_{n(AB)} & A_{n(AA)} & A_{n(BB)} \end{bmatrix} \begin{bmatrix} J_{AB} \\ J_{AA} \\ J_{BB} \end{bmatrix} = \begin{bmatrix} E_1 - E_0 \\ \vdots \\ E_n - E_0 \end{bmatrix} \quad (4.2)$$

4.2.1 Magnetite

The magnetite crystal structure was created by using atomic positions determined from the most recent set of neutron diffraction data (*Fleet*, 1981). The symmetry of the magnetite lattice gives rise to a primitive unit cell which can be described by a single A site atom with a multiplicity of 2 and a single B site atom with a multiplicity of 4 (space group $Fd3m$). This system has two independent magnetic atoms, which only allow two unique spin configurations to be calculated, far below the 10-20 configurations desired for a good estimate of exchange energies, and only half of the minimum of four required to estimate J_{AA} , J_{AB} and J_{BB} . Therefore, the symmetry of the lattice was explicitly broken to create a structure with enough independent magnetic atoms to generate the required number of spin configurations. The iron atoms in the unit cell were defined to be degenerate with other iron atoms on the same layer (in the z direction), but not iron atoms on other layers. This led to a structure which had eight independent magnetic atoms, one for each

z layer in the unit cell, with a multiplicity of 2 for A site atoms and a multiplicity of 4 for B site atoms (spacegroup $Pmm2$). From this structure, 256 spin configurations can be calculated.

The coefficients of the nearest neighbour exchange energies for each of these configurations were then computed from the Hamiltonian, and the majority of the configurations were found to yield the same coefficients as other configurations. Degenerate cases were discarded, and the remaining 18 spin configurations were selected for calculation. Table 4.1 gives the details of the 18 spin configurations and corresponding coefficients of J_{ij} .

Table 4.1: Details of the 18 unique spin configurations for magnetite and the corresponding coefficients of J_{ij} . Atoms 1-4 correspond to A sites on the spinel lattice, and atoms 5-8 correspond to B sites. Configuration I is the ferromagnetic case, and configuration II is the ferrimagnetic case. Other cases correspond to more complex spin configurations.

Atom #	Spin configuration								Exchange coefficients		
	1	2	3	4	5	6	7	8	$A_{n(AB)}$	$A_{n(AA)}$	$A_{n(BB)}$
I	↑	↑	↑	↑	↑	↑	↑	↑	-1080	-200	-486
II	↑	↑	↑	↑	↓	↓	↓	↓	1080	-200	-486
III	↑	↑	↑	↑	↓	↑	↓	↑	0	-200	162
IV	↓	↑	↓	↑	↑	↑	↑	↑	0	200	-486
V	↓	↑	↓	↑	↓	↑	↓	↑	0	200	162
VI	↑	↑	↑	↑	↑	↑	↓	↓	0	-200	-162
VII	↑	↑	↑	↑	↑	↓	↓	↓	540	-200	-162
VIII	↑	↑	↑	↓	↑	↑	↑	↑	-540	0	-486
IX	↑	↑	↑	↑	↑	↑	↑	↓	-540	-200	-162
X	↓	↑	↑	↑	↓	↑	↑	↑	-360	0	-162
XI	↓	↓	↑	↑	↑	↑	↑	↑	0	0	-486
XII	↓	↓	↑	↑	↓	↑	↑	↑	0	0	-162
XIII	↓	↑	↑	↑	↑	↑	↓	↑	-180	0	-162
XIV	↓	↑	↑	↑	↓	↑	↓	↑	0	0	162
XV	↑	↓	↑	↓	↑	↑	↑	↓	0	200	-162
XVI	↑	↓	↓	↓	↑	↑	↑	↑	540	0	-486
XVII	↑	↓	↓	↓	↑	↑	↑	↓	180	0	-162
XVIII	↑	↑	↑	↓	↑	↓	↓	↓	360	0	-162

Test calculations were carried out to determine the optimal number of k-points and value of $RK_{\max}$. Calculations were performed on ferrimagnetic magnetite (case II) with convergence conditions on energy of 0.0001 Ry and charge of 0.0001 e. Optimisation of atomic positions was not performed as the forces on each atom in the lattice remained small (< 10 mRy/Bohr). When testing the convergence of $RK_{\max}$, the number of k-points was fixed at 500. When testing the

convergence of the number of k-points, $RK_{\max}$ was fixed at $RK_{\max} = 7$. Results from these tests can be found in Figure 4.1. Energy was found to be sufficiently converged for a value of $RK_{\max} = 9$ and 500 k-points.

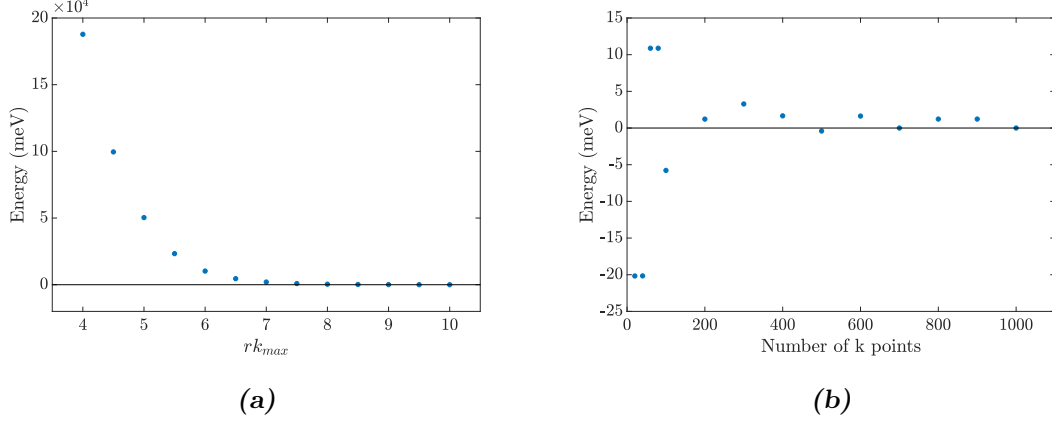


Figure 4.1: Total energy against: (a) $RK_{\max}$ for a fixed value of 500 k-points, and (b) number of k-points for a fixed value of $RK_{\max} = 7$ for the $Pmm2$ magnetite structure. Energies are given in meV relative to (a) $RK_{\max} = 10$ and (b) 1000 k-points. The solid line donates $E = 0$ in both sub-figures. In (a) the total energy can be seen to converge for increasing $RK_{\max}$. In (b) the total energy can be seen to fluctuate by 3 – 5 meV (corresponding to 0.06 – 0.1 meV per atom) with increasing number of k-points.

4.2.2 Maghemite

The maghemite crystal structure was created by using the experimental atomic positions of *Shmakov et al.* (1995) to make a supercell of size $1 \times 1 \times 3$ unit cells. Vacancies were created in the 4b Wyckoff positions using the full ordered vacancy structure of the $P4_12_12$ spacegroup (*Shmakov et al.*, 1995; *Grau-Crespo et al.*, 2010). This leads to a structure which possesses nine unique Fe atoms; three of which correspond to A sites in the spinel lattice and six which correspond to B sites. From this structure, 512 different spin configurations can be made, of which 100 of these have unique coefficients of J_{ij} within the Heisenberg Hamiltonian. Nineteen of these structures were selected for calculation including the ferrimagnetic ground-state case, and the ferromagnetic case. Table 4.2 gives details of the spin configurations and the values of the exchange coefficients for each configuration.

Testing of the convergence of total energy of the system was again undertaken for the number of k-points and the value of $RK_{\max}$ (Figure 4.2). Calculations were performed on the ferrimagnetic spin configuration for systems with a range of values of $RK_{\max}$ where the number of k-points was fixed to 80, and for a range of k-points where the value of $RK_{\max}$ was fixed at $RK_{\max} = 7$. Convergence conditions for the energy were set to 0.0001 Ry and charge to 0.0001 e and geometry

Table 4.2: Details of the 19 selected spin configurations for maghemite and corresponding coefficients of J_{ij} . Atoms 1-3 correspond to A sites on the spinel lattice, and atoms 4-9 correspond to B sites. Configuration I is the ferromagnetic case, and configuration II is the ferrimagnetic case. Other cases correspond to more complex spin configurations.

Atom #	Spin configuration									Exchange coefficients		
	1	2	3	4	5	6	7	8	9	$A_{n(AB)}$	$A_{n(AA)}$	$A_{n(BB)}$
I	↑	↑	↑	↑	↑	↑	↑	↑	↑	-3000	-600	-1200
II	↑	↑	↑	↓	↓	↓	↓	↓	↓	3000	-600	-1200
III	↓	↓	↓	↓	↓	↓	↓	↓	↑	-2400	-600	-600
IV	↓	↓	↓	↓	↓	↓	↓	↑	↑	-1800	-600	-200
V	↓	↓	↓	↓	↓	↓	↑	↓	↑	-1200	-600	0
VI	↓	↓	↓	↓	↓	↓	↑	↑	↑	-600	-600	400
VII	↓	↓	↓	↓	↓	↑	↑	↓	↑	0	-600	400
VIII	↓	↓	↓	↓	↓	↑	↑	↑	↑	600	-600	400
IX	↓	↓	↓	↓	↑	↑	↑	↓	↑	-1200	-600	-200
X	↓	↓	↓	↓	↑	↑	↑	↑	↑	1800	-600	-200
XI	↓	↑	↑	↑	↑	↓	↑	↑	↑	-1000	0	-400
XII	↓	↑	↓	↓	↓	↓	↓	↓	↑	-800	200	-600
XIII	↓	↓	↑	↓	↑	↓	↑	↓	↑	-400	0	-200
XIV	↓	↑	↓	↓	↓	↑	↓	↑	↑	-200	200	200
XV	↓	↓	↑	↓	↓	↑	↑	↑	↑	200	0	400
XVI	↓	↑	↓	↓	↑	↑	↑	↓	↑	400	200	-200
XVII	↓	↓	↑	↑	↑	↑	↓	↓	↑	800	0	200
XVIII	↓	↑	↓	↑	↑	↑	↑	↑	↑	1000	200	-1200
XIX	↓	↓	↓	↑	↑	↑	↑	↓	↑	2400	-600	-800

optimisation was performed in all cases. Due to computational restraints caused by the size of the maghemite supercell simulations had to be run at the lowest acceptable accuracy. Energy was found to be sufficiently converged for 80 k-points, and a value of $RK_{\max} = 8$ was chosen as the largest practical size given computational restraints.

4.3 Results and discussion

4.3.1 Magnetite

Calculations on magnetite were performed on the 18 spin configurations described in Table 4.1. Previous studies on magnetite using Wien2k have determined that a value of $U = 3.8$ eV gives

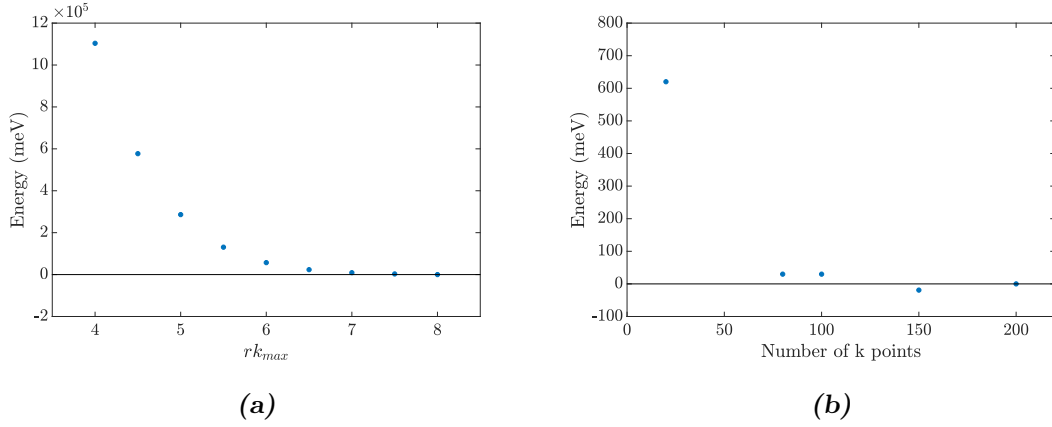


Figure 4.2: Total energy against: (a) RK_{max} for a fixed value of 80 k-points and (b) number of k-points for a fixed value of $RK_{max} = 7$ for the $P4_12_12$ maghemite structure. Energies are given in meV relative to (a) $RK_{max} = 8$ and (b) 200 k-points. The solid line donates $E = 0$ in both sub-figures. In (a) the total energy can be seen to converge for increasing RK_{max} . In (b) the total energy can be seen to fluctuate by 25 meV (corresponding to 0.15 meV per atom) for systems with 80 k-points or greater.

material properties which agree well with experiment (Bliem *et al.*, 2014). Calculations were performed with a range of values of $U = 0.0, 3.0$ and 3.8 eV.

The magnetic moment of the unit cell in each configuration was found to agree well with the theoretical value of the moment, which is calculated by assuming a moment of $5\mu_B$ on A sites and $4.5\mu_B$ on B sites (Table 4.3). The forces on the atoms in each spin configuration were found to be small (< 10 mRy/Bohr) indicating that the experimental atomic structure is very close to the DFT ground state and so optimisation of atomic positions was not performed. In agreement with the known magnetic structure of magnetite (Shull *et al.*, 1951), the ferrimagnetic spin configuration corresponded to the lowest energy magnetic state.

Least-squares fitting was applied to the spin configurations using values for the coefficients of J_{AB} , J_{AA} and J_{BB} from Table 4.1 for each value of U . The values of exchange energies extracted from the least squares method are shown in Table 4.4. Figure 4.3 shows a plot of the energy of each spin configuration from the DFT calculations where $U = 3.8$ eV (taken from Table 4.3) against the energy of the spin configuration calculated using the equation for the exchange energy term in the Heisenberg model,

$$E_J = -2 \sum_{\langle ij \rangle} S_i S_j J_{ij}, \quad (4.3)$$

where J_{ij} are the best fit values for exchange energy from the least squares fitting for $U = 3.8$ eV. The energies are shown relative to the total energy of the ferrimagnetic spin configuration. If both DFT and the Heisenberg model were an exact description of reality, then for each spin

Table 4.3: Details of magnetic moment per unit cell and energy for the 18 spin configurations calculated for magnetite. The theoretical moment, the moment obtained from the $U = 3.8$ eV DFT calculations and the difference, Δ , is given for each configuration. The energy of each configuration relative to the ferrimagnetic groundstate is also shown for each value of U used in this study. Energies are only comparable to configurations with the same value of U , i.e., the energy of the ferrimagnetic configuration is not the same across different values of U . Entries which are blank correspond to configurations which failed to converge and are omitted from the least-squares fitting.

	Moment (μ_B)			Energy (meV)		
	Theory	DFT	Δ	U = 0.0	U = 3.0	U = 3.8
I	112	112.00	0.00	10732.5	6862.8	5331.8
II	-32	-32.00	0.00	0	0	0
III	40	38.60	1.40	5292.7	3362.3	2507.0
IV	72	72.00	0.00	5056.7	-	-
V	0	0.00	0.00	5104.6	-	2358.4
VI	40	39.04	0.96	5111.0	3375.9	2502.4
VII	4	3.96	1.04	2710.9	1622.4	1570.5
VIII	92	92.00	0.00	7951.2	4938.5	3952.5
IX	76	75.08	0.92	7861.4	5137.2	3904.1
X	56	56.00	0.00	6653.6	4349.7	3568.6
XI	72	72.00	0.00	5152.9	3129.1	2429.2
XII	36	36.00	0.00	4788.4	3121.6	2432.9
XIII	56	55.24	0.76	5781.8	3824.6	3010.4
XIV	20	19.54	0.46	4998.9	3159.7	2385.4
XV	36	36.00	0.00	4882.1	3130.5	2478.8
XVI	52	52.00	0.00	2437.3	1452.7	1172.3
XVII	16	16.46	-0.46	4015.5		1867.4
XVIII	-16	-16.00	0.00	3355.2		1628.2

configuration $E_{\text{DFT}} = E_J$ would hold true, and all points on the plot would lie on the line $y = x$. Thus the better the fit of a linear relationship between E_{DFT} and E_J , the closer the agreement is between the two models. As discussed by *Blukis* (2018), a better agreement between E_{DFT} and E_J is not a sufficient test of good J_{ij} values, however, a good fit is required to give confidence that the DFT calculations can be successfully mapped onto the Heisenberg model.

Figure 4.3 shows good agreement between the E_{DFT} and E_J . The dashed line shows the best linear fit to the data, which gives an equation of $y = 1.00x - 1.11$ with a coefficient of determination (R^2) value of 0.992, indicating a very good fit. Similar plots have been produced for values of

$U = 0.0$ and 3.0 eV (not shown), with the results detailed in Table 4.4. In all cases, the line of best fit is very close to the ideal $y = x$ line and the R^2 value is in excess of 0.99.

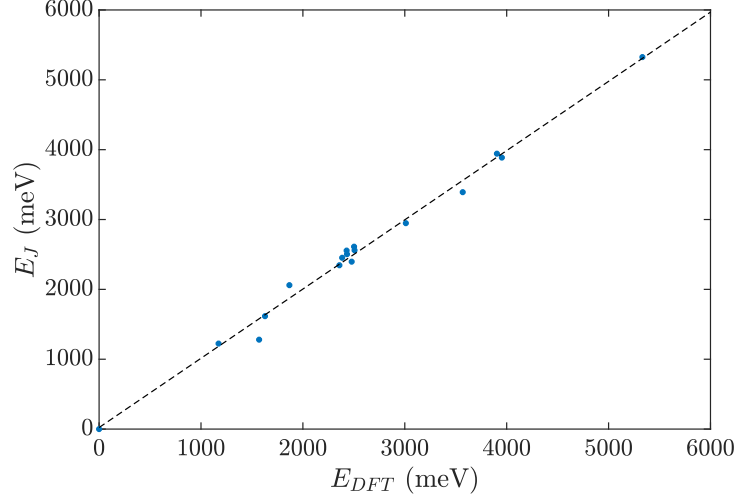


Figure 4.3: Energy of each spin configuration from DFT calculations plotted against the energy of each configuration from the Heisenberg model using best fit values of J_{ij} . Energy is relative to the ferrimagnetic configuration for calculations where $U = 3.8$ eV. The black dashed line is the line of best fit to the data, which recovers values of $m = 1.00$ and $c = -1.11$ with $R^2 = 0.992$.

Table 4.4: Best fit values of J_{ij} for nearest neighbour exchange energies in magnetite for $U = 0.0$, 3.0 and 3.8 eV. Also included are details of the line of best fit (in the form $y = mx + c$) and the coefficient of determination (R^2) value of that fit of E_{DFT} against E_J which can be used as a measure of the success of mapping the DFT calculations onto the Heisenberg model.

U (eV)	J_{AB} (meV)	J_{AA} (meV)	J_{BB} (meV)	m	c	R^2
0.0	-4.91	-0.81	-0.22	1.00	-0.31	0.997
3.0	-3.16	-0.93	-0.08	0.99	29.7	0.999
3.8	-2.47	-0.54	-0.16	1.00	-1.11	0.992

The values of J_{AB} , J_{AA} and J_{BB} follow some general trends independent of the value of U applied to the system. The J_{AB} exchange energy is the strongest interaction and is of an antiferromagnetic nature, which will lead to the known ferrimagnetic ordering of magnetite. The J_{AA} interaction is a weaker antiferromagnetic interaction, in agreement with the predictions of superexchange (Anderson, 1950). The value of J_{BB} is small and antiferromagnetic in all cases. J_{AB} , J_{AA} and J_{BB} are plotted against U in Figure 4.4. J_{AB} has a strong dependence on the value of U , with its magnitude decreasing linearly with increasing value of U . The values of J_{AA} and J_{BB} remain broadly constant with changing U .

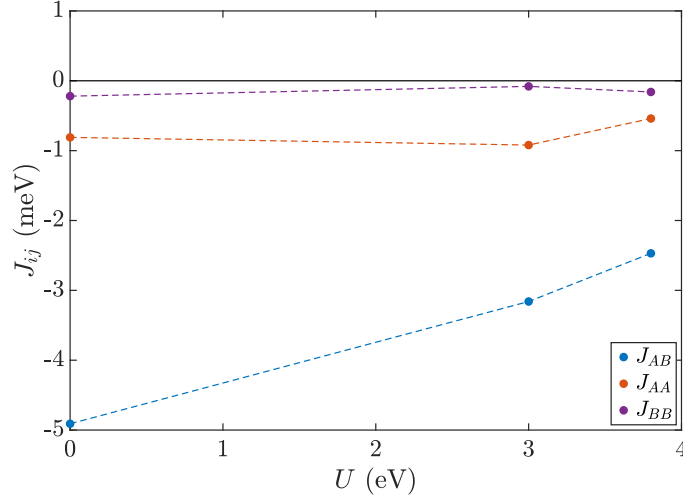


Figure 4.4: J_{AB} , J_{AA} and J_{BB} against U . The magnitude of J_{AB} decreases linearly with increasing U , whilst the values of J_{AA} and J_{BB} remain broadly constant.

Comparison of exchange energies with previous estimates

For each of the sets exchange energies listed in Table 4.5 the Curie temperature of magnetite was estimated using the Monte Carlo model described in section 2.3. The Hamiltonian used to estimate T_C included exchange and cubic anisotropy terms and was given by,

$$\mathcal{H} = -2 \sum_{\langle ij \rangle} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j - K_V \sum_i (S_{i,x}^2 S_{i,y}^2 + S_{i,y}^2 S_{i,z}^2 + S_{i,x}^2 S_{i,z}^2) \quad (4.4)$$

where $S_A = 2.5$, $S_B = 2.25$ and $K_V = 0.002$ meV per spin (Mazo-Zuluaga *et al.*, 2008). For each simulation a system $10 \times 10 \times 10$ unit cells in size was generated and periodic boundary conditions were applied. Values of magnetisation and susceptibility were calculated in temperature steps of 20 K with an equilibration period of 10,000 MC steps and an averaging period of 10,000 MC steps at each temperature step. T_C was taken as the temperature at which the maximum value of susceptibility occurred.

The most recent experimental study of exchange energy in magnetite was made by Bourdonnay *et al.* (1971). This work gave values which agree well with the relative magnitudes and types of interaction expected from super-exchange theory (Anderson, 1950), and also the slightly earlier study of Möglestue (1968). The value of J_{AB} in these studies agrees well with the value obtained using a Hubbard potential of $U = 3.8$ eV in this work. The J_{AA} interaction is stronger in magnitude in the experimental work compared to the $U = 3.8$ eV case, but both are weaker than the J_{AB} interaction. In all three cases the value of J_{BB} is small in magnitude, but ferromagnetic in the experimental estimations and antiferromagnetic in this study. The Curie temperatures from Monte Carlo simulations of all three set of J_{ij} are similar (620-660 K) and ~ 200 K lower than the Curie temperature of magnetite.

Table 4.5: Comparison of nearest neighbour exchange energies in magnetite between previous studies and this work. The Curie temperature for the corresponding set of values of J_{ij} obtained from Monte Carlo modelling is also shown. The experimental value for the Curie temperature in magnetite is 850 K (Pauthenet and Bochirol, 1951).

	J_{AB} (meV)	J_{AA} (meV)	J_{BB} (meV)	T_C (K)
Néel (1948)	-2.0	-1.5	0.04	480
Möglestue (1968)	-2.42	-1.52	0.31	620
Bourdonnay et al. (1971)	-2.38	-1.56	0.26	600
Uhl and Siberchicot (1995)	-2.92	-0.11	0.63	900
U = 0.0 eV	-4.91	-0.81	-0.22	1340
U = 3.0 eV	-3.16	-0.93	-0.08	840
U = 3.8 eV	-2.47	-0.54	-0.16	660

Later work by Uhl and Siberchicot (1995) using *ab initio* techniques to model spin spiral configurations led to a set of values which differ from the previous experimental studies. Whilst a dominant antiferromagnetic J_{AB} interaction is observed, a very weak antiferromagnetic J_{AA} interaction and stronger ferromagnetic J_{BB} interaction is also predicted. This is in contrast to both previous work and the expectations of superexchange theory. However, these values of J_{ij} have been used in the literature for subsequent Monte Carlo modelling of magnetite as they yield a Curie temperature close to the experimental value (Mazo-Zuluaga et al., 2008; Evans et al., 2015). This study has found that a value of $U = 3.0$ eV for the Hubbard parameter leads to a Curie temperature of 840 K which is in good agreement with the experimental result of 850 K (Pauthenet and Bochirol, 1951). In addition, the relative magnitudes of the values of J_{ij} agree more closely with superexchange theory than the results obtained by Uhl and Siberchicot (1995). These values may therefore offer some improvement over those of Uhl and Siberchicot (1995) with regards to usage in Monte Carlo simulations.

4.3.2 Maghemite

The presence of vacancies in the maghemite structure leads to large forces on many of the atoms inside the unit cell. Geometry optimisation must therefore be performed to find the optimal atomic positions. Two different methods were used here to resolve the forces on atoms in maghemite.

1. Geometry optimisation was applied to each of the 19 spin configurations to find optimised atomic positions for each case. This method guarantees that the atomic positions for each configuration are optimised, but may lead to inconsistencies between positions and thus total energies in different spin configurations.
2. Geometry optimisation was applied to the ground state ferrimagnetic spin configuration

(configuration II). This atomic structure was then used in calculations of other spin configurations (with no geometry optimisation). This method guarantees that atomic positions are consistent across spin configurations, but may lead to large forces on atoms within the unit cell if atoms are not sufficiently close to their optimised positions.

Table 4.6: Details of magnetic moment and energy per $3 \times 1 \times 1$ supercell for the 19 spin configurations calculated using methods 1 and 2 for maghemite. The theoretical moment, the moment obtained from $U = 0.0$ eV DFT calculations and the difference, Δ , is given for each configuration. The energy of each configuration relative to the ferrimagnetic groundstate is also shown. The percentage of atoms in the maghemite supercell with forces greater than 10 mRy/Bohr using method 2 is given in the final column.

	Moment (μ_B)			Energy (meV)		% atoms
	Theory	DFT	Δ	Method 1	Method 2	Method 2
I	320	224.00	96.00	24636.7	-	-
II	-80	-80.00	0.00	0	0	0.0
III	-280	-200.00	-80.00	20328.7	-	-
IV	-240	-176.00	-64.00	17704.8	-	-
V	-200	-152.00	-48.00	17004.0	-	-
VI	-160	-128.00	-32.00	14202.3	-	-
VII	-120	-112.00	-8.00	12322.5	-	-
VIII	-80	-80.00	0.00	9333.6	12049.1	52.5
IX	-40	-32.00	-8.00	6791.6	-	-
X	0	0.00	0.00	4119.5	5318.5	47.5
XI	160	128.00	32.00	15865.3	-	-
XII	-200	-160.00	-40.00	17609.0	-	-
XIII	-40	-40.00	0.00	16695.5	18694.7	47.5
XIV	-80	-80.00	0.00	14523.3	17597.1	52.5
XV	0	0.00	0.00	9445.8	12119.1	50
XVI	40	40.00	0.00	10067.5	11999.0	55
XVII	40	40.00	0.00	5992.3	8661.3	45
XVIII	160	160.00	0.00	11440.8	12337.1	20
XIX	40	40.00	0.00	1895.9	2470.4	15

For method 1, calculations were run for all 19 spin configurations for a value of $U = 0.0$ eV. The magnetic moments from the DFT calculations were compared to the theoretical moment expected for that configuration assuming a moment per atom of $5\mu_B$ (Table 4.6). Of the 19 configurations modelled, nine of these had DFT moments which did not agree with the theoretical value. As the coefficients of J_{ij} in Table 4.2 are computed using the theoretical moment, these nine configurations were excluded from the least-squares fitting. For method 2, calculations were only run for the 10 configurations which showed agreement with the theoretical value. Good agreement between moments was still seen in all cases.

Least-squares fitting was performed for both sets of calculations and the energy E_J plotted against E_{DFT} using the same procedure as with magnetite (Figure 4.5). The data was found to be a poor fit to the Heisenberg model, with R^2 values of 0.55 for method 1 and 0.56 for method 2. This is in sharp contrast to the high quality fits found for magnetite where $R^2 > 0.99$. The values of J_{ij} obtained from the fitting are also inconsistent with the magnitudes of the expected values. In particular, method 1 yields best fit exchange energies which suggest a ferromagnetic structure with a very high Curie temperature, despite the DFT calculations (and experimental observation) demonstrating that a ferrimagnetic structure is the magnetic groundstate for maghemite. The least squares method has therefore been unable to extract estimates for exchange energies in maghemite due to difficulties resolving the vacancies in a manner which allow for energies to be mapped onto the Heisenberg model. Further calculations were not performed with values of $U = 3-4$ eV as the problem with applying the least squares method arises due to the different optimal position of each atom in different spin configurations and this was unlikely to be resolved by applying a Hubbard potential.

Table 4.7: Best fit values of J_{ij} for nearest neighbour exchange energies in maghemite for method 1 and method 2. Also included are details of the line of best fit (in the form $y = mx + c$) of E_{DFT} against E_J which can be used as a measure of the success of mapping the DFT calculations onto the Heisenberg model.

	J_{AB} (meV)	J_{AA} (meV)	J_{BB} (meV)	m	c	R^2
Method 1	6.09	23.70	8.69	0.92	-31.96	0.55
Method 2	-1.91	15.82	-3.12	0.88	-27.78	0.56

Despite the failure of this part of my PhD to obtain estimates for J_{ij} in $\gamma\text{-Fe}_2\text{O}_3$, it should be noted that this Chapter describes work undertaken over a period of two years. A number of technical difficulties arose on the Imperial HPC facility as a result of the design of Wien2k and this required a considerable amount of testing of the code and collaboration with the Research Computing Service to resolve. In addition, the magnetite and maghemite structures themselves posed a computational challenge due to their size, and so a lot of effort was expended to minimise the size of the calculations to reduce computational time. In spite of this, the work here still

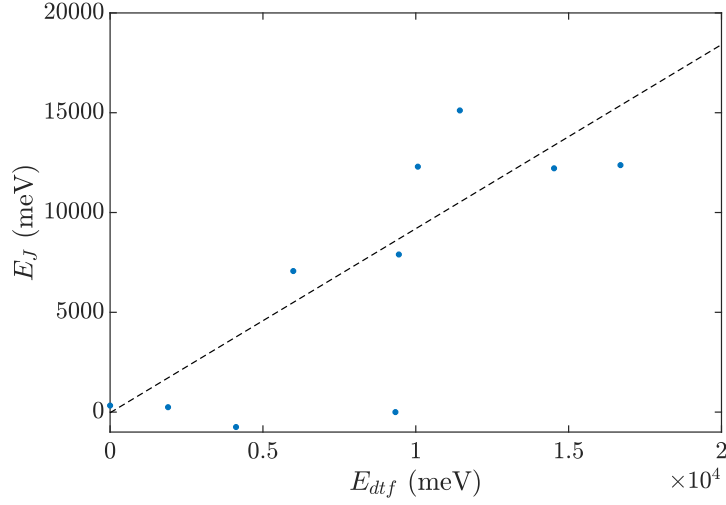


Figure 4.5: Energy of each spin configuration from DFT calculations plotted against the energy of each configuration from the Heisenberg model using best fit values of J_{ij} . Energy is relative to the ferrimagnetic configuration for calculations using method 1. The black dashed line is the line of best fit to the data, which recovers values of $m = 0.92$ and $c = -32.0$ with $R^2 = 0.55$.

represents a total job time in excess of 15,000 CPU days. Other techniques for estimating J_{ij} using DFT (e.g. using spin spirals *Uhl and Siberchicot* (1995)) were not investigated due to time constraints.

4.4 Conclusions

Exchange energies in magnetite were estimated using the least squares method for a range of values for the Hubbard parameter. A value of $U = 3.8$ eV, as used in previous DFT studies of magnetite, estimated exchange energies close to the values of J_{ij} obtained from experimental studies. However, the value of $T_C = 660$ K recovered from Monte Carlo simulations using these exchange energies does not agree with the experimental value of 850 K. Exchange energies estimated using $U = 3.0$ eV made a good prediction of $T_C = 840$ K from Monte Carlo simulations, with the relative magnitudes of these values of J_{ij} closer to those predicted from superexchange than the widely used values from *Uhl and Siberchicot* (1995). We therefore suggest that these new values may offer an improvement to Monte Carlo simulations over the values obtained by *Uhl and Siberchicot* (1995). Attempts to estimate exchange energies in maghemite failed due to difficulties resolving the vacancies in a manner which allow for energies to be mapped onto the Heisenberg model.

Chapter 5

Monte Carlo modelling core-shell of magnetic nanoparticles

5.1 Introduction

The low-temperature oxidation of magnetite (Fe_3O_4) to maghemite ($\gamma\text{-Fe}_2\text{O}_3$) is ubiquitous in nature and often occurs as a weathering process under natural atmospheric conditions (*Prévot et al.*, 1981; *van Velzen and Dekkers*, 1999; *Liu et al.*, 2004, 2010). The oxidation of magnetite initially occurs at the surface, where Fe^{2+} ions are either partially removed from the crystal or react with oxygen, and are converted to Fe^{3+} to form a new crystal layer (*O'Reilly*, 1984). Thereafter, Fe^{2+} ions diffuse to the surface, leaving vacancies in the interior, where they oxidise and lead to the growth of the particle (*Sidhu et al.*, 1977). At low temperatures, this process leads to the development of a steep oxidation gradient, in which the surface of a grain or particle of magnetite is oxidised to maghemite, and the core is composed of stoichiometric magnetite (*Gallagher et al.*, 1968; *Askill*, 1970). This gives rise to a core-shell structure, with a core of magnetite surrounded by a shell of less magnetic maghemite.

At the nanoscale, the magnetic behaviour of magnetite-maghemite core-shell particles is likely to be complex due to the effects of finite size on Curie temperature (e.g. *Wang et al.*, 2011b; *Li et al.*, 2014) and coercivity (e.g. *Iglesias and Labarta*, 2001; *Mazo-Zuluaga et al.*, 2009) coupled with the partial oxidation of these particles. Understanding how this collectively changes the magnetic behaviour of these particles is of interest due to nanoscale magnetite's widespread presence in rock magnetic samples and the environment, in addition to its use as a material in biomedical applications (*Evans and Heller*, 2003; *Pankhurst et al.*, 2009).

The magnetic behaviour of magnetite-maghemite core-shell particles has seen numerical investigation on the micrometre scale (*Ge et al.*, 2014), but studies on the nanoscale have to date been limited to experimental investigations into the composition, structure and basic magnetic proper-

ties of these particles (*Santoyo Salazar et al.*, 2011; *Frison et al.*, 2013). In particular, *Frison et al.* (2013) were able to study core-shell particles down to 6 nm in size and found a linear decrease in saturation magnetisation against the ratio of R_{shell}/R as shell thickness was increased.

In this Chapter, the Heisenberg Monte Carlo model described in section 2.3 is used to study nanoscale magnetite-maghemite core-shell particles with a diameter in the range of 4.8-12 nm. The effect of increasing oxidation on the Curie temperature and hysteresis properties of core-shell particles is investigated. Additionally, the finite-size scaling of Curie temperature in nanoscale particles with simple cubic, bcc and spinel crystal structures is studied and compared to the results of the mean-field modelling in Chapter 3 and previous work.

5.2 Details of the model

5.2.1 Monte Carlo model

The Heisenberg Monte Carlo model described in section 2.3 was applied to systems with simple cubic and bcc crystal structures, and models for magnetite, maghemite and magnetite-maghemite core-shell particles. The model considered the effect of exchange, magnetocrystalline anisotropy and external field. The corresponding Hamiltonian is given by (e.g. *Mazo-Zuluaga et al.*, 2008; *Nedelkoski et al.*, 2017),

$$\mathcal{H} = -2 \sum_{\langle ij \rangle} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j - K_V \sum_i (S_{i,x}^2 S_{i,y}^2 + S_{i,y}^2 S_{i,z}^2 + S_{i,x}^2 S_{i,z}^2) - g \mu_B \mathbf{H} \cdot \sum_i \mathbf{S}_i, \quad (5.1)$$

where $\mathbf{S}_i$ is the spin of site i , J_{ij} is the isotropic exchange interaction between sites i and j defined such that ferromagnetic exchange is positive, K_V is the first order cubic magnetocrystalline anisotropy constant, $g \approx 2$ is the gyromagnetic ratio, μ_B is the Bohr magneton and $\mathbf{H}$ is an external field acting on each site. Simple cubic and bcc particles were initialised with a spin of $|\mathbf{S}| = 1$ applied to each site, an exchange energy of $J = 5$ meV between each nearest neighbour and with no anisotropy (i.e. $K_V = 0$). Model parameters for magnetite and maghemite are discussed in section 5.2.3.

Mazo-Zuluaga et al. (2008, 2009) studied the effect of surface anisotropy on the hysteresis properties of magnetite nanoparticles by varying the ratio $\frac{K_S}{K_V}$ between values of $-3500 < \frac{K_S}{K_V} < 3500$. Whilst the coercivity of magnetite nanoparticles was found to increase as the ratio $\frac{K_S}{K_V}$ was increased, this effect was found to be negligible for the values of $\frac{K_S}{K_V} \leq 10$. The value of K_S is typically an order of magnitude larger than K_V (*Berger et al.*, 2008). In view of this, surface anisotropy was not expected to alter the behaviour of the core-shell nanoparticles and was neglected in the modelling undertaken here.

In order to simulate the bulk-like properties of each different material, periodic boundary conditions were applied to systems of a size large enough to minimise finite-size effects. When

studying finite-size particles, both cubic and spherical particle shapes were considered. Spherical particles were approximated by including an atom in the particle if it lay within $\frac{d}{2}$ of the centre of the particle, where d is the diameter of a particle.

Simulations of magnetisation curves and hysteresis loops were performed. At each temperature or hysteresis step, the system used the final state of the previous step and was left to settle into equilibrium for 10,000 Monte Carlo steps (see section 2.3.1 for details). Values for magnetisation, susceptibility, energy and specific heat obtained were computed over a further 10,000-30,000 Monte Carlo steps, depending on system size. Each system was modelled over an ensemble of 12-32 CPU cores, with a different random number seed used to generate the trial spins in each system in the ensemble. The values of magnetisation, susceptibility, energy and specific heat were then averaged over the ensemble to further improve the statistics of the modelling.

5.2.2 Determining T_C

In Monte Carlo simulations of bulk materials the Curie temperature is typically determined in one of three ways: (1) as the temperature for which the maximum value of susceptibility occurs, (2) as the temperature at which the intersection of Binder's U_4 cumulant (equation 2.55) occurs for periodic systems of different sizes, (3) or by fitting the magnetisation data to the equation,

$$m(T) = \left(1 - \frac{T}{T_C}\right)^\beta \quad (5.2)$$

where m is the normalised magnetisation and β is a critical exponent with a value of $\beta = 0.33$. In section 2.3.2 the Curie temperature of simple cubic and bcc systems were found using Binder's U_4 cumulant method and shown to be in very good agreement with previous high fidelity Monte Carlo simulations (*Chen et al.*, 1993). The U_4 method is therefore used here to determine the bulk Curie temperature, $T_C(\infty)$. Using this approach, a value of $T_C(\infty) = 167$ K can be obtained for the simple cubic system, $T_C(\infty) = 239$ K for the bcc system.

When modelling nanoscale systems, neither Binder's cumulant method, nor fitting to equation (5.2) are suitable approaches for identifying T_C . Binder's cumulant method is reliant upon periodic boundary conditions being applied to systems of many sizes and so cannot be applied to finite-size systems. Fitting to equation (5.2) is not reliable, because in finite-size systems there is both: (a) a large residual magnetisation above the Curie temperature, and (b) no guarantee that the value of β is unchanged when modelling systems that are not bulk-like. This leaves using the peak in susceptibility to identify the transition temperature as the remaining method for determining T_C .

In finite-sized systems, the divergence in quantities such as specific heat and susceptibility associated with a phase transition are rounded due to the finite size of thermodynamic quantities such as the free energy (Figure 5.1) (*Binder*, 1987). When studying the susceptibility in MC simulations, instead of a sharp peak at T_C , a broader and noisy peak is instead observed. The noise is due to fluctuations in the value of susceptibility, which is similar across a range of temperatures

in finite systems, and arises from the random sampling which underpins Monte Carlo methods. This means that accurately determining the temperature at which the phase transition occurs is potentially difficult. The underlying statistics of the sampling and averaging can be improved by increasing the number of averaging steps at each temperature and running an ensemble of simulations with different random number seeds, but computational restraints limit the gains obtainable through this approach. Further reduction in fluctuations of susceptibility close to the phase transition can be achieved by applying a moving average filter (Figure 5.1) to the raw data where the moving average, $\bar{y}_n$, is computed over a window of five data points,

$$\bar{y}_n = \frac{y_{n-2} + y_{n-1} + y_n + y_{n+1} + y_{n+2}}{5}. \quad (5.3)$$

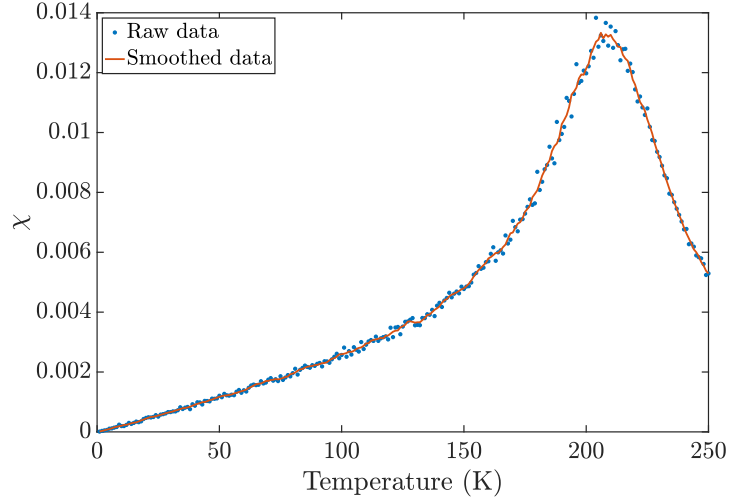


Figure 5.1: Susceptibility, χ , against temperature for a $14 \times 14 \times 14$ cubic bcc particle, with $|\mathbf{S}_i|$ and $J_{ij} = 5$ meV. The system has been run with averages calculated over 10,000 MC steps with an ensemble of 12 random number seeds. The raw values of susceptibility are shown by the blue circles, and the smoothed data shown by the red line. A reduction in the fluctuation of χ near the phase transition can be seen in the smoothed data.

5.2.3 Magnetite and maghemite

Magnetite and maghemite particles were generated on a spinel crystal structure using a two sub-lattice model. Vacancies in the $4b$ Wyckoff positions of maghemite were created using the fully ordered vacancy structure (Shmakov *et al.*, 1995; Grau-Crespo *et al.*, 2010), which minimises the Coulomb repulsion between the atoms on the occupied $4b$ positions.

In magnetite the magnitude of the spin on each sub-lattice was set to $|\mathbf{S}_A| = 2.5$ and $|\mathbf{S}_B| = 2.25$. Nearest neighbour exchange energies of $J_{AB} = -2.92$ meV, $J_{AA} = -0.11$ meV and $J_{BB} = 0.63$ meV were taken from Uhl and Siberchicot (1995) and a cubic anisotropy constant of $K_V =$

0.002 meV/spin (Aragón, 1992) was used, in line with previous studies (Mazo-Zuluaga *et al.*, 2008; Evans *et al.*, 2015).

In maghemite, the magnitudes of the spins on each sub-lattice are equal, where $|\mathbf{S}_A| = |\mathbf{S}_B| = 2.5$. A value of cubic anisotropy constant of $K_V = 0.0008$ meV/spin was obtained from previous experimental work (Hou *et al.*, 1998). In the absence of experimental or numerical estimates of J_{ij} values in maghemite, estimates were made using relative values of T_C between magnetite and maghemite. The experimental Curie temperatures of magnetite and maghemite are 850 K and ~ 950 K (1.1 times that of magnetite) respectively (Dunlop and Özdemir, 1997). The exchange energies from Uhl and Siberchicot (1995) give a value from Monte Carlo simulations of $T_C(\infty) = 907$ K in magnetite. The next step is therefore to make a sensible estimate of J_{ij} in maghemite which obtains a value close to $T_C(\infty) = 1110$ K (~ 1.1 times that of magnetite). During oxidation from magnetite to maghemite there is no electronic or structural change to the A sites of the spinel lattice. Therefore it seems reasonable to assume the J_{AA} is the same or very similar in both materials. The value of J_{AA} in maghemite was therefore set to the same value as used for magnetite. Whilst the B sites do undergo electronic and structural change during oxidation, the J_{BB} interaction contributes only 10% of the energy of that of the J_{AB} interaction. It would therefore need to undergo a very large change in magnitude in order to make any real change to the value of T_C , and so is also set to the value used for magnetite. The Curie temperature of magnetite obtained from Monte Carlo simulations in Chapter 4 shows a linear dependence with respect to the strength of the principle J_{AB} interaction (Figure 5.2). T_C was therefore estimated in maghemite using values of J_{AB} equal to 1.0, 1.1, 1.2 and 1.3 times the J_{AB} value in (Uhl and Siberchicot, 1995), and values of $J_{AA} = -0.11$ and $J_{BB} = 0.63$. A value of $J_{AB} = -3.21$ meV (equal to 1.1 times the value in magnetite) was found to give a Curie temperature of $T_C = 1100$ K, close to the desired value. Parameter values for magnetite and maghemite are summarised in Table 5.2.

Table 5.1: Model parameters for magnetite and maghemite used in this study; magnitude of sub-lattice spins $|\mathbf{S}_A|$ and $|\mathbf{S}_B|$, nearest neighbour exchange energies J_{AB} , J_{AA} and J_{BB} , and cubic magnetocrystalline anisotropy constant, K_V (Valstyn *et al.*, 1962; Aragón, 1992; Uhl and Siberchicot, 1995).

	$ \mathbf{S}_A $	$ \mathbf{S}_B $	J_{AB} (meV)	J_{AA} (meV)	J_{BB} (meV)	K_V (meV)
Fe_3O_4	2.5	2.25	-2.92	-0.11	0.63	0.002
$\gamma\text{-Fe}_2\text{O}_3$	2.5	2.5	-3.21	-0.11	0.63	0.0008

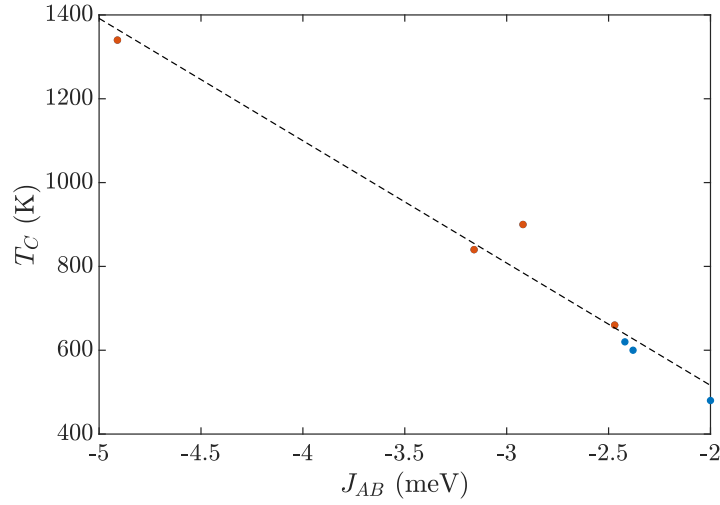


Figure 5.2: T_C from Monte Carlo simulations against J_{AB} for a range of experimental and numerical estimates of J_{ij} in magnetite. The blue points correspond to experimental values of J_{ij} from Néel (1948), Möggestue (1968) and Bourdonnay *et al.* (1971), and the red points correspond to numerical values of J_{ij} from Chapter 4 and Uhl and Siberchicot (1995). The dashed line is the line of best fit to the data, and is used to demonstrate the linear dependence of T_C on the strength of J_{AB} .

5.2.4 Creating magnetite-maghemite core-shell particles

Magnetite-maghemite core-shell particles were generated with a cubic shape of size d unit cells along its edge. The core of the particle consisted of a cube of magnetite of size, d_{core} , with a shell of maghemite which had a thickness of t unit cells (Figure 5.3). The unit cells of maghemite and magnetite were assumed to be the same size; defects arising from the mismatch in size of the unit cell ($\sim 1\%$) were ignored.

Whilst the values of J_{ij} in magnetite and maghemite have already been discussed, a further set of nearest neighbour interactions occur across the boundary between the material core and shell material. As J_{AA} and J_{BB} were set to be equal in magnetite and maghemite in this study, they were also set to remain the same across the boundary, leaving the J_{AB} interaction as the term which needs further consideration. For each pair of unit cells which form part of the boundary between the core and the shell, i.e. one face of a unit cell in the core which is in contact with one face of a unit cell in the shell, the total contribution to the exchange energy from the J_{AB} interaction between two unit cells is $32S_A S_B J_{AB}$. By considering particles of different diameters and shell thicknesses, the percentage of exchange interaction due to J_{AB} which occurs across the boundary can be found. This percentage is at a maximum for a thin shell of one unit cell thickness, as the surface area of the core is largest, and does not rise above 1.4% for any size of core-shell particles (the maximum value occurs when $d = 6$). It is therefore clear that the exchange across

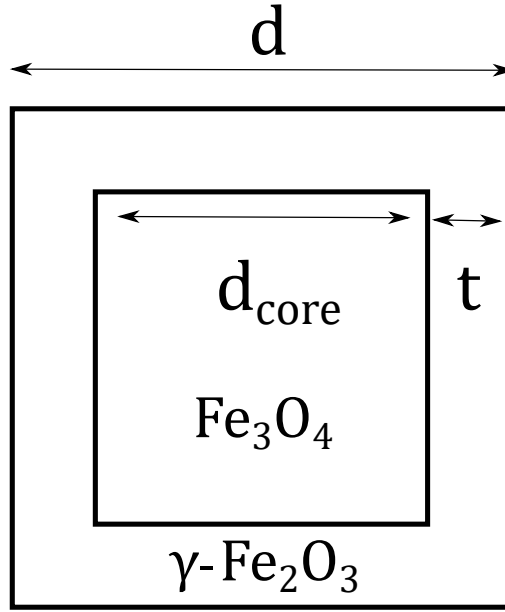


Figure 5.3: Schematic of a slice through a magnetite-maghemite core-shell particle as modelled in this study. The core consisted of a cube of magnetite of size d_{core} unit cells surrounded by a shell of maghemite of thickness t unit cells. The total width of the particle was $d = d_{\text{core}} + 2t$. Particles were modelled in states of increased oxidation in which the thickness of the shell was gradually increased.

the boundary is a minor contribution to the total exchange. To test this, two simulations were performed on a core-shell particle where $d = 6$ and $t = 1$. J_{AB} across the boundary was fixed to that of magnetite in one simulation and maghemite in the other. No appreciable difference was found between the magnetisation curves of the two systems, suggesting that there is little sensitivity to choice of J_{AB} . As a result, for all further simulations, J_{AB} across the boundary was chosen to be equal to the value of J_{AB} in magnetite.

5.3 Effect of size on Curie temperature

Finite-sized scaling in simple cubic, bcc and magnetite nanoparticles was studied using the MC model and compared with the results of the mean-field model used in Chapter 3 and previous computational and experimental studies. As previously discussed, the Curie temperature of particles of finite size is reduced due to the growth of the correlation length being limited by the smallest dimension of the system and the reduction in Curie temperature obeys a finite-size scaling relationship (equation 3.1).

In Chapter 3, I studied finite-sized scaling in magnetic nanoparticles using the mean-field approximation and obtained values of ν in the range 0.46-0.55 for simple cubic, bcc and magnetite

nanoparticles with a range of shapes. These results were consistently close to the mean-field value of $\nu = 0.5$.

A similar approach was taken here to obtain values for ν in the Monte Carlo model. Spherical and cubic particles of a range of sizes were modelled, and their Curie temperatures identified from a maximum in the susceptibility. Using the same approach as before, values for ν were calculated by non-linear least squares regression to equation (3.1) using the Levenberg-Marquardt algorithm (*Levenberg, 1944*) and the error in ν was taken as the 95% confidence interval of the best fit value. Particles of different materials and shapes were considered separately. Fitting was undertaken initially on all sizes of particles from a particular system, and then by successively removing the smallest particle from the fit. The final value of ν was taken as the one with the smallest error, in order to account for any deviation from scaling behaviour seen at small sizes.

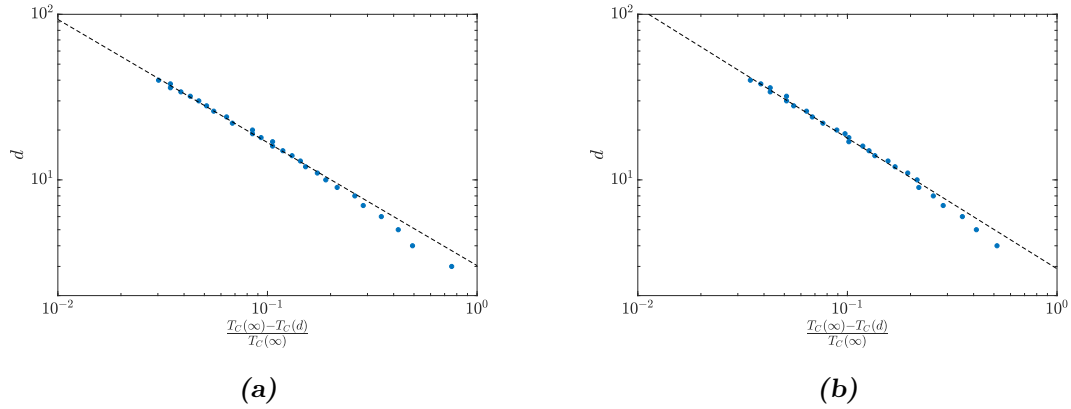


Figure 5.4: Example fits to determine the value of the scaling exponent ν for; (a) cubic and (b) spherical bcc particles. The dashed lines show the best fits to equation (3.1) where the error in ν is minimised.

Table 5.2: Best fit values of ν for simple cubic, bcc and magnetite particles with cubic and spherical shapes.

	Simple cubic	Body centred cubic	Magnetite
Cube	0.85 ± 0.04	0.73 ± 0.02	0.67 ± 0.05
Sphere	0.79 ± 0.04	0.78 ± 0.03	0.66 ± 0.07

Figure 5.9 shows examples of the fits to the scaling equation for bcc particles. In all cases there is a good fit to equation (3.1), with some deviation away from the fit at very small particle sizes. A value of $\nu = 0.66$ is found for Fe_3O_4 particles, close to the value expected for the 3D Heisenberg model. A previous study by *Wang et al. (2011b)* obtained a value of $\nu = 0.82 \pm 0.02$ for Fe_3O_4 from data initially collected during MC modelling by *Mazo-Zuluaga et al. (2008)*. However, the data in that study corresponded to particles < 5 nm in size. This discrepancy between two Monte

Carlo models of magnetite which are using the same values for J_{ij} is typical of the difficulty that has been had in obtaining consistent scaling results in nanoscale particles across many studies.

Cubic bcc particles also recover a value of $\nu = 0.73$ close to the theoretical value of $\nu = 0.7$. However the results for spherical bcc, and cubic and spherical sc particles are in less good agreement. The smallest seven particles were removed from the fit of the spherical bcc system, as these particles show clear deviation away from scaling (Figure 5.9) and an improved value of $\nu = 0.76 \pm 0.03$ was obtained. The same procedure was applied to both shapes of sc particle and a value of $\nu = 0.83 \pm 0.06$ for cubes and $\nu = 0.77 \pm 0.05$ for spheres was obtained. Why the cubic sc system exhibits an elevated value of ν is unclear, as the previously suggested mechanisms for systems which exhibit larger than expected scaling exponents, namely long range ordering (*Lyberatos et al.*, 2012) and surface dislocations (*Wang et al.*, 2011a) do not apply in this case.

The values of ν found by fitting to equation (3.1) using the MC model have shown a larger spread of values compared to the results obtained in Chapter 3. Values of the scaling exponent obtained by the mean-field model lie within 10% of the analytical mean-field value, whilst the corresponding values obtained using the MC model lie within 18.5% of the 3D Heisenberg value. However, the value of $\nu = 0.83 \pm 0.06$ obtained for sc cubic particles may be considered an outlying result, and if this is discarded then the values of ν in the MC model also lie within 10% of the expected value. Overall, nanoscale systems investigated using the MC model have shown that the value of ν found by fitting a range of systems to the finite-size scaling equation compares well to the value of ν expected in the 3D Heisenberg model.

5.4 Comparison between the mean-field and Monte Carlo models

Whilst the mean-field and Monte Carlo modelling approaches predict many of the same qualitative behaviours, there are quantitative differences in results which can be compared. The value of the Curie temperature predicted by the two modelling methods is different, with the mean-field approach typically predicting higher Curie temperatures. For example, in bulk magnetite using values of exchange energies taken from *Uhl and Siberchicot* (1995), the mean-field model predicts a value of $T_C = 1616$ K well above the experimentally determined value of 850 K. In comparison, the Monte Carlo method predicts a value of $T_C = 900$ K, much closer to the accepted value. This difference between the methods is generally attributed to the effect of the correlations between spins in magnetic materials. These correlations are neglected in the mean-field approach, but actually play an important role in magnetic ordering at temperatures close to T_C .

The values of the scaling exponent ν calculated in both the mean-field and Monte Carlo models are close to the expected values of ν in the respective universality class of each model in almost all cases. Re-arranging the the scaling equation (3.1) to the form,

$$\frac{T_C(d)}{T_C(\infty)} = 1 - \left(\frac{d_0}{d}\right)^{\frac{1}{\nu}} \quad (5.4)$$

it is possible to see that larger values of the scaling exponent will result in larger (relative) reductions in Curie temperature due to size. This effect can be seen in Figure 5.5, where magnetite particles modelled using the Monte Carlo model show a greater relative reduction in T_C for their size compared to magnetite particles modelled using the mean-field model.

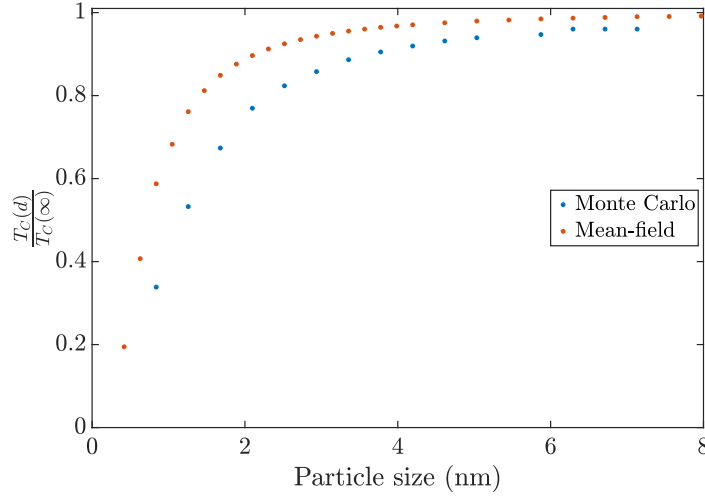


Figure 5.5: $\frac{T_C(d)}{T_C(\infty)}$ plotted against particle size for cubic magnetite particles with J_{ij} taken from Uhl and Siberchicot (1995). Particles have been modelled using the mean-field and Monte Carlo models. A greater reduction in $T_C(d)$ for particles modelled using the Monte Carlo method can be seen.

One of the initial aims of the Monte Carlo modelling was to also investigate the effect of shape on Curie temperature in order to understand any differences in results between the mean-field and Monte Carlo approaches. However the susceptibility of particles with a more elongated shape did not show any clear peak, instead fluctuating with increasing temperature. No coding bug could be found as the source of this effect, and there was not sufficient time within the scope of this project to either investigate this further or find an alternative method of estimating T_C in these systems.

5.5 Magnetite-maghemite core-shell particles

5.5.1 Properties of core-shell particles

Magnetisation curves (Figure 5.6a) were calculated for core-shell particles of size $9 \times 9 \times 9$ unit cells (7.6 nm). The magnetisation is normalised to the saturation magnetisation of a pure Fe_3O_4 particle. A reduction in normalised magnetisation with increasing oxidation can be seen, with the

normalised magnetisation a pure $\gamma\text{-Fe}_2\text{O}_3$ particle equal to the expected value of 0.83 times the normalised magnetisation of Fe_3O_4 . The shape of the magnetisation curves is similar in all cases, with a roughly linear decrease in magnetisation at lower temperatures, before an increase in the reduction of magnetisation as the temperature approaches T_C .

An increase in Curie temperature with increasing oxidation can be seen from both the magnetisation curves and the susceptibility plots (Figure 5.6b). Peaks in the susceptibility are larger in the partially oxidised particles than in either of the pure magnetite or maghemite end members, likely due to the interaction between the two phases.

The magnetisation and susceptibility of the core and shell of a partially oxidised $6 \times 6 \times 6$ (5.0 nm) particle is shown in Figure 5.7. The core and shell are strongly coupled together, with the peak in susceptibility in both core and shell aligning well with the peak in total susceptibility. This is seen in particles with both an approximately even quantity of Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$ and particles which have in excess of 90% $\gamma\text{-Fe}_2\text{O}_3$, and suggests that the surface area of the contact between the core and the shell does not alter the coupled magnetic behaviour of the particles.

5.5.2 Effect of oxidation on Curie temperature

Figure 5.8a shows the Curie temperatures of core-shell particles as a function of fraction of maghemite for particles of size $d = 6, 9, 12$ and 15 unit cells in width. In all cases a non-linear relationship between T_C and fraction of $\gamma\text{-Fe}_2\text{O}_3$ can be seen. This contrasts with the linear relationship seen in experimental and MC studies of hematite-ilmenite solid solutions, where a linear relationship between T_C and fraction of ilmenite is seen (*Dunlop and Özdemir, 1997; Harrison, 2006*). However, there are key differences between the two systems, namely that the particles here are of finite-size, have two clearly ordered phases, and that those phases have a contact area which is itself dependent upon the degree of oxidation of the particle. The strong coupling between the core and shell of these particles shown in Figure 5.7 suggests that the contact area may not play such an important role in determining T_C .

When considering the ratio of $T_C(d)$ in magnetite and maghemite particles from the finite-size scaling equation (3.1) the following expression is obtained,

$$\frac{T_{C_{\text{Fe}_3\text{O}_4}}(d)}{T_{C_{\gamma\text{-Fe}_2\text{O}_3}}(d)} = \frac{T_{C_{\text{Fe}_3\text{O}_4}}(\infty) \Phi_{\text{Fe}_3\text{O}_4}}{T_{C_{\gamma\text{-Fe}_2\text{O}_3}}(\infty) \Phi_{\gamma\text{-Fe}_2\text{O}_3}}, \quad (5.5)$$

where

$$\Phi = 1 - \left(\frac{d_0}{d} \right)^{\frac{1}{\nu}}. \quad (5.6)$$

Magnetite and maghemite share very similar crystal structures, which in this model have the same size of lattice parameter. If the values of ν and d_0 in magnetite and maghemite are sufficiently close in value then equation (5.5) can be simplified to,

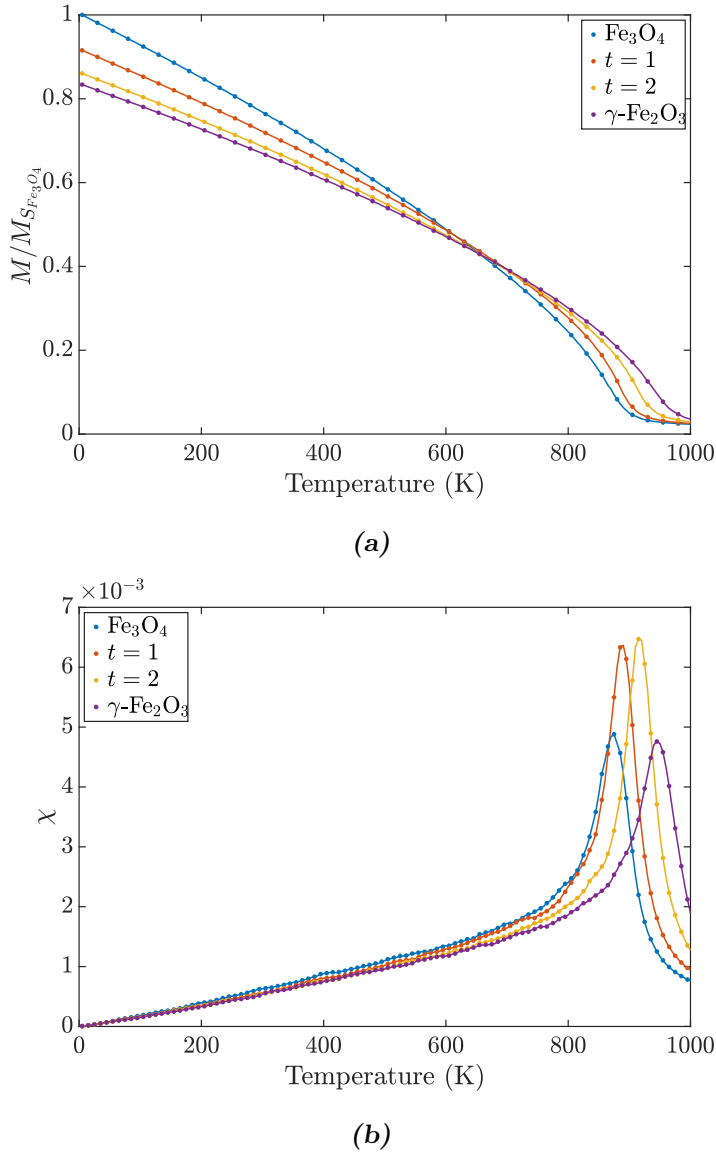


Figure 5.6: (a) Magnetisation curves for core-shell particles of 7.6 nm ($9 \times 9 \times 9$ unit cells) in size. Magnetisation is normalised against the saturation magnetisation of a pure Fe_3O_4 particle. (b) Susceptibility against temperature plots for the same particles. Plotted curves are for Fe_3O_4 particles with shell thicknesses of $t = 1$ and $t = 2$ unit cells (0.84 nm and 1.68 nm respectively), and a particle of fully oxidised $\gamma\text{-}Fe_2O_3$.

$$\frac{T_{C_{Fe_3O_4}}(d)}{T_{C_{\gamma\text{-}Fe_2O_3}}(d)} = \frac{T_{C_{Fe_3O_4}}(\infty)}{T_{C_{\gamma\text{-}Fe_2O_3}}(\infty)}. \quad (5.7)$$

The ratio of the bulk Curie temperature in magnetite and maghemite is therefore preserved between two particles of the same size. In Figure 5.8b the Curie temperatures of each particle of size, d , were normalised to the Curie temperature of a pure Fe_3O_4 particle of the same size. In agreement with equation (5.7), the Curie temperatures of the maghemite particles are consistently

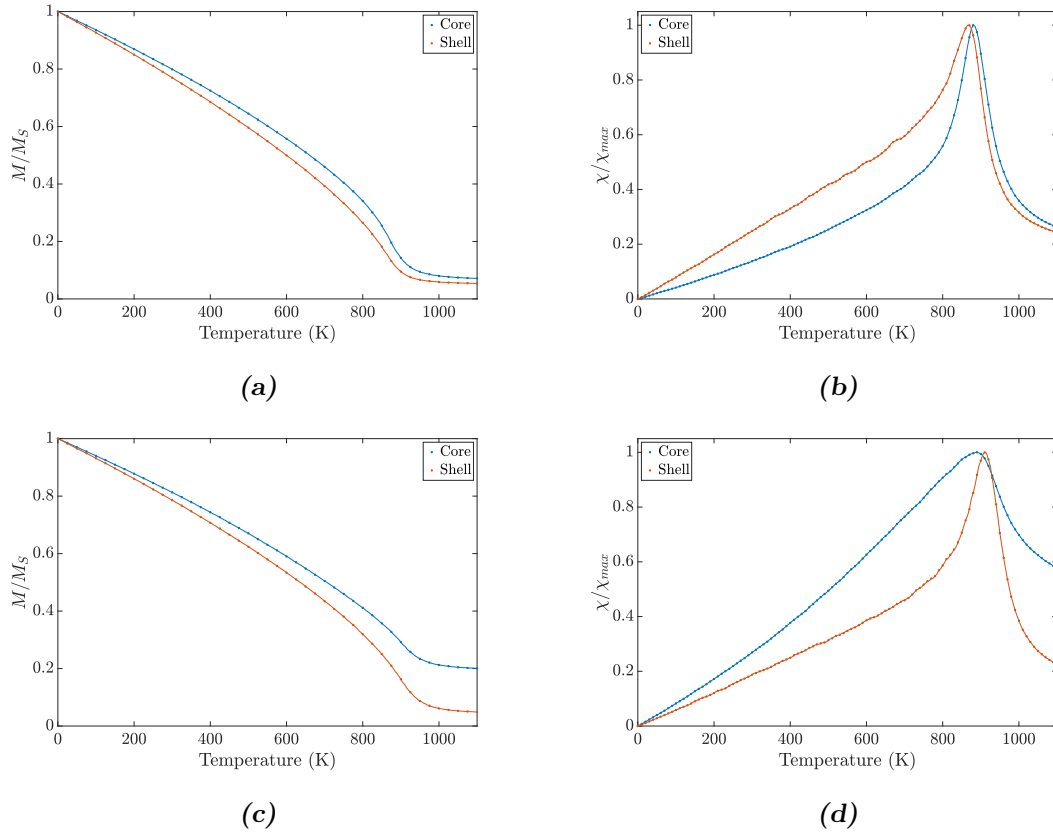


Figure 5.7: (a) Normalised magnetisation curves and (b) susceptibility plots for the magnetite core and maghemite shell of a 5.0 nm ($6 \times 6 \times 6$ unit cells) particle with a shell of thickness $t = 1$. (c) Normalised magnetisation curves and (d) susceptibility plots for the magnetite core and maghemite shell of a 5.0 nm ($6 \times 6 \times 6$ unit cells) particle with a shell of thickness $t = 2$.

~ 1.1 times those of the magnetite particles, in agreement with the ratios of the bulk values of T_C . It also becomes apparent that the normalised Curie temperatures of partially oxidised particles all collapse onto a single curve. Independent of particle size, the relative increase in T_C as a function of percentage oxidation is the same.

The following mechanism for this behaviour is proposed. When a core-shell particle has a thin shell of maghemite, many of the atoms in the shell will be on the surface and so have a reduced number of nearest neighbours. This reduces the increase in T_C that would normally be observed due to the presence of the maghemite phase. As the thickness of the shell increases, the maghemite atoms which form part of the shell consist of those on the surface and also those with a full complement of nearest neighbours towards the centre of the particle. This, coupled with the reducing number of magnetite atoms, results in a faster increase in T_C as the fraction of maghemite approaches one.

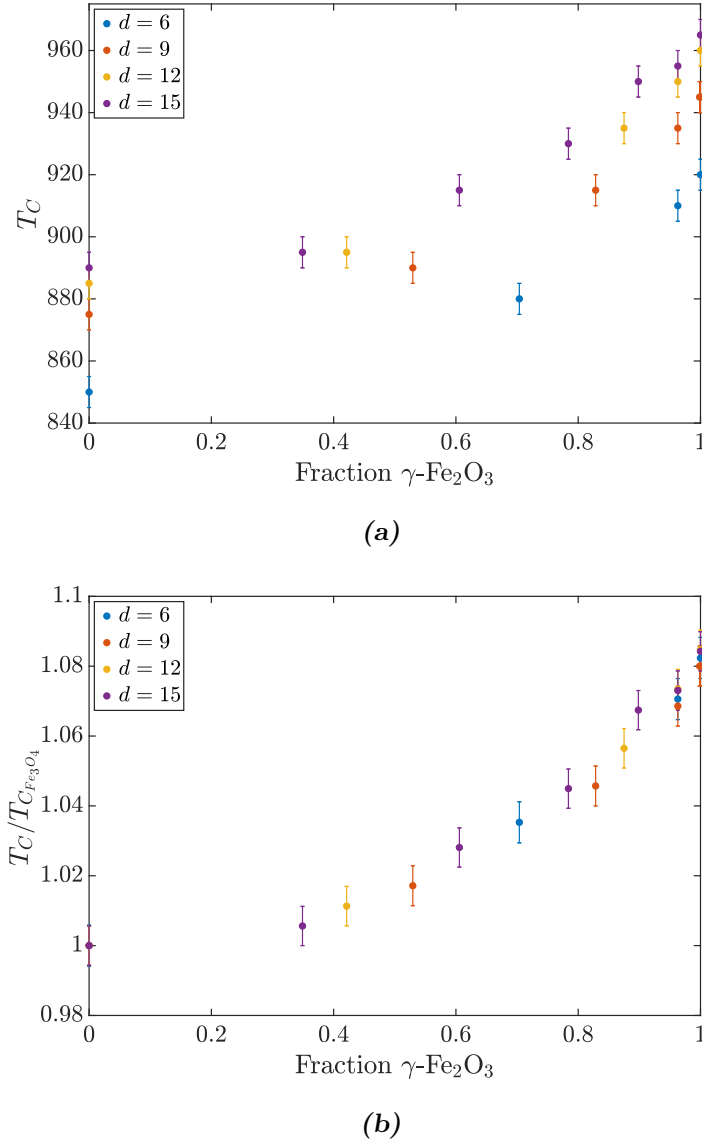


Figure 5.8: (a) Curie temperature against fraction maghemite for core-shell particles of size $d = 6, 9, 12$ and 15 unit cells in size. (b) Normalised Curie temperature against fraction of maghemite for core-shell particles of size $d = 6, 9, 12$ and 15 unit cells in size.

5.5.3 Effect of oxidation on hysteresis

The low-temperature hysteresis properties of magnetite-maghemite core-shell particles in the size range $d = 5.0\text{--}10.1$ nm were investigated by applying an external field along the $[111]$ easy direction of the magneto-crystalline anisotropy at a temperature of 1 K, chosen to minimise thermal effects. The field strength was varied in from $-2.5 - 2.5$ T in steps of 0.05 T. All plots show normalised magnetisation against external field to allow easy comparison between results.

The hysteresis properties of bulk-like magnetite and maghemite show that magnetite has a higher coercivity of $B_C = 1.64$ T than maghemite where $B_C = 1.31$ T (Figure 5.9a). These values

for B_C retrieved from the MC model are approximately two orders of magnitude larger than the coercivity of magnetite. However, coercivity in MC simulations is dependent upon both the algorithm used for selecting trial spins and the number of averaging steps (*Nehme et al.*, 2015), and so numerical results are not guaranteed to match experiment. This dependence on algorithm is highlighted when considering the MC study of *Mazo-Zuluaga et al.* (2009) on magnetite, in which trial spins were selected using only a random spin direction. The choice of a trial spin with random direction requires the system to overcome a large energy penalty from the exchange term due to the temporary breaking of the preferential magnetic order to ultimately align with the external field. As a result, the coercivity of the system is ~ 90 T. This method of selecting trial spins would be expected to show a strong dependence of B_C on the values of exchange interaction. The method of choosing spins in the Monte Carlo model used here applies a set of trial spins, one of which restricts the trial spin to a cone about the current spin direction. This allows the spins of the system to rotate in the presence of an external field without causing the temporary change in the magnetic ordering of the material. As a result, the coercivity is greatly reduced, and the magnetocrystalline anisotropy constant becomes the controlling factor in determining B_C in the system.

Nanoscale particles of magnetite and maghemite exhibit a lower coercivity than bulk-like systems, with B_C increasing as particle size increases (Figure 5.9b) in agreement with previous work (*Iglesias and Labarta*, 2001).

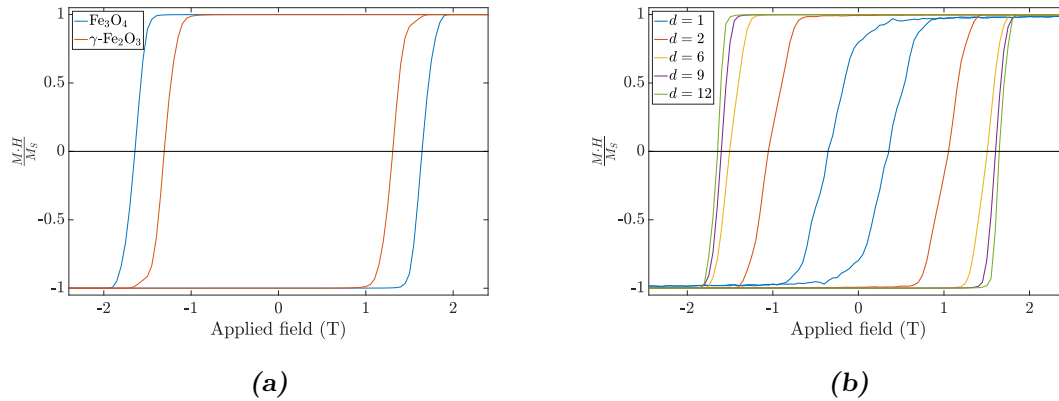


Figure 5.9: Hysteresis loops for; (a) bulk Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$, and (b) Fe_3O_4 particles with a range of diameters.

Hysteresis loops were calculated for magnetite-maghemite core-shell particles of size $d = 6, 9$ and 12 unit cells, which corresponds to a real particle sizes of $d = 5.0, 7.6$ and 10.1 nm. For a given particle size, coercivity was largest for a particles of pure magnetite, and then decreased as the thickness of the maghemite shell increased (Figure 5.10). For 5.0 and 7.6 nm particles B_C is found to decrease linearly with the fraction of maghemite found in that particle as the particle oxidises (Figure 5.11). For the largest 10.1 nm particle slightly different behaviour is observed. An overall

decrease in coercivity with increasing oxidation can be seen, but for core-shell particles with a fraction of maghemite greater than 0.8, the coercivity shows little change in value for increasing oxidation. The particle with the lowest fraction of oxidation (~ 0.4), has a coercivity close to that of pure magnetite. Computational restraints meant that hysteresis loops of the 10.1 nm particle could only be conducted with an ensemble of four different random number seeds, as opposed to the ensemble of 32 used in all other simulations. When the fraction of maghemite is high (low), the core-shell systems are more similar to the particles of pure maghemite (magnetite), with many of the atoms being identical between the different particles. As the same set of random number seeds are used in each set of simulations, this may lead to any bias in the results arising from a small ensemble size being replicated across each particle. Alternatively, this may be a physical result arising from the size of the particle, in which the greater number of maghemite or magnetite atoms present in a larger system have a bigger influence on the overall behaviour of the particle. However similar behaviour is not seen in the Curie temperature data for a 10.1 nm system, in which an ensemble size of 32 was used, suggesting that the result is probably numerical in origin.

Maghemite has a tetragonal superstructure, and so its anisotropy is uniaxial in nature. However, a cubic anisotropy was applied to maghemite in this model. In the hysteresis loops presented here, the external field has been applied along the $[1, 1, 1]$ easy direction of cubic anisotropy in magnetite. This difference in treatment of MCA may lead to higher coercivities being predicted in this model compared to one applying uniaxial anisotropy to maghemite, as the uniaxial anisotropy term will lower the overall energy barrier between the $[1, 1, 1]$ and $[-1, -1, -1]$ directions. However, the same trend of reduction in coercivity with increasing oxidation would still be expected in both cases.

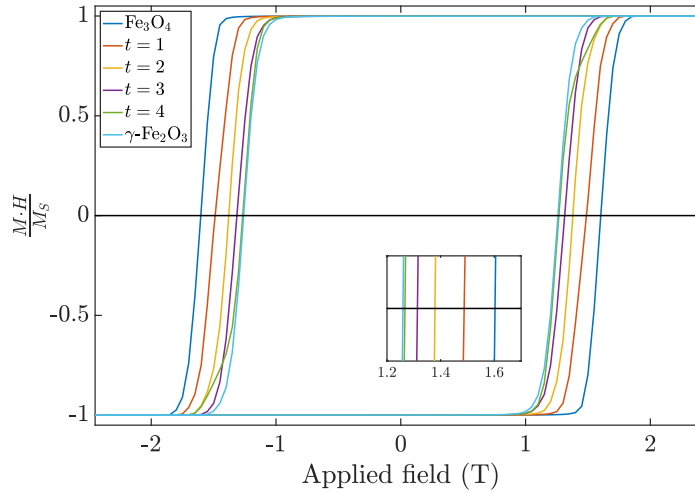


Figure 5.10: Hysteresis loops for a $9 \times 9 \times 9$ (7.6 nm) core-shell particle with progressing oxidation from pure Fe_3O_4 to $\gamma\text{-Fe}_2\text{O}_3$. Inset is the section of the hysteresis loop from 1.2-1.7 T highlighting B_C .

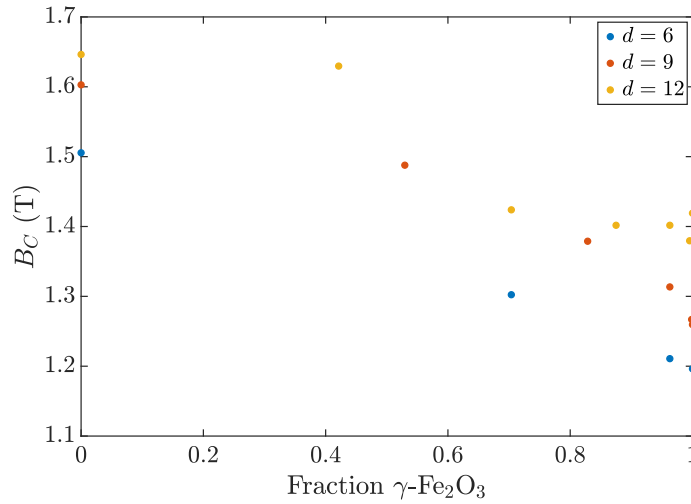


Figure 5.11: Coercivity against fraction $\gamma\text{-Fe}_2\text{O}_3$ for a range of particle sizes.

Comparison to previous studies

Ge et al. (2014) studied partially oxidised core-shell particles in the size range 40-120 nm using both experimental and micromagnetic modelling techniques. Characterisation of the experimental particle samples revealed a lognormal distribution with a bias towards larger single domain (SD) particles of diameter ~ 50 nm, suggesting a dominance of SD particles within the sample. The coercivity of the samples showed an increase in B_C as the fraction of maghemite increased to ~ 0.9 , before exhibiting a drop in coercivity above this.

In order to draw better comparison between the results of the MC model to the micromagnetic modelling of *Ge et al.* (2014) the magnetic parameters used in each case are first compared. *Ge et al.* (2014) used values of $M_S = 4.8 \times 10^5 \text{ Am}^{-1}$ for magnetite and $M_S = 3.8 \times 10^5 \text{ Am}^{-1}$ for maghemite taken from previous experimental studies. The Monte Carlo model used the theoretical magnetic moments for each atom, which corresponds to values of $M_S = 5.0 \times 10^5 \text{ Am}^{-1}$ for magnetite and $M_S = 4.2 \times 10^5 \text{ Am}^{-1}$ for maghemite. The slightly lower values for M_S used in the micromagnetic simulations are likely due to the presence of magnetic domains in the larger samples used for measuring M_S experimentally. The values of the anisotropy constant K_V used by *Ge et al.* (2014) correspond to an anisotropy energy of 0.002 meV per spin for magnetite and 0.0008 meV per spin for maghemite, which are the same as the values used in the Monte Carlo simulations. The general good agreement between parameter values suggests that comparison between the two methods can be reasonably made.

Micromagnetic simulations of 40-60 nm single domain particles predicted a decrease in B_C with oxidation. Larger pseudo-single domain (PSD) particles showed more complex behaviour, but with a general trend of increased B_C with increasing oxidation. A weighted average of the modelling results was performed to match the log-normal distribution of particle samples and

predicted little change in the value of B_C with oxidation until the particle completely oxidised, when a reduction in coercivity was seen. They suggested the difference between the modelling and experimental results may be down to a number of factors, including the failure of the model to consider micro-structural effects such as cracking or stresses at the core-shell boundary, and possible underestimation of the oxidation parameter in the experimental samples. The results of this study agree with the numerical results obtained by *Ge et al.* (2014) for single domain particles, namely that B_C decreases in single domain systems with increasing oxidation.

5.6 Conclusions

Partially oxidised magnetite-maghemite core-shell nanoparticles in the size range 5.4 - 12.6 nm have been studied using a Monte Carlo model. The Curie temperature of these particles were found to increase non-linearly with increasing oxidation, likely due to the dominance of the surface in reducing the number of nearest neighbours in the maghemite shell at low levels of oxidation. Hysteresis loops of core-shell particles were calculated, and the coercivity of a particle was found to decrease with the fraction of maghemite in the particle. Studies investigating magnetic hyperthermia treatment typically use nanoparticles of magnetite to heat tumours using hysteresis (*Pankhurst et al.*, 2003). This finding suggests that the partial oxidation of these nanoparticles will lead to lower coercivities, and so reduce the amount of heating obtainable through hysteresis. Finite-sized scaling in simple cubic, bcc and magnetite particles was also investigated. Values of the scaling exponent ν in the range 0.66-0.77 were found in most cases to be in good agreement with the theoretical value.

Chapter 6

Conclusions

This thesis presents an investigation into a number of properties of magnetic nanoparticles using numerical methods and a range of different modelling techniques. The effect of particle size and shape on the Curie temperature of magnetic nanoparticles was investigated in Chapter 3, numerical estimates of exchange energies in iron oxides were made in Chapter 4 and the magnetic properties of iron oxide core-shell nanoparticles were investigated in Chapter 5.

In Chapter 3 magnetic nanoparticles were studied using a mean-field model to investigate the effect of particle size and shape on the Curie temperature of those particles. The theory of finite-size scaling of the Curie temperature of nanoparticles has been established for many years (*Fisher and Ferdinand*, 1967), and whilst good agreement between theory and experiment has been seen in thin films (*Huang et al.*, 1993; *Ambrose and Chien*, 1996), this is not the case for nanoparticles. Whilst some experimental studies of magnetite and hematite have recovered values for the scaling exponent, ν , close to the theoretical value (*Wang et al.*, 2011b; *Li et al.*, 2014), other experimental and numerical studies have recovered values of the scaling exponent which do not agree well with theory (*Iglesias and Labarta*, 2001; *Wang et al.*, 2011a; *Lyberatos et al.*, 2012). In addition to the lack of clarity on the scaling behaviour of nanoparticle systems, to my knowledge no studies on the effect of shape on the Curie temperature of magnetic nanoparticles had been conducted.

A numerical mean-field model of magnetic nanoparticles was developed, and simple cubic, bcc and magnetite particles were created with cubic, spherical and needle-like shapes. The Curie temperatures of particles with the same smallest length, d , were found to vary with shape (Figure 3.3). Spherical particles were found to have the lowest Curie temperature with cubic, 2:1:1, 5:1:1 and 10:1:1 needles having successively higher values of T_C . The difference in Curie temperature between 10:1:1 and spherical particles, ΔT_C , was found to be 15-25% of the value of $T_C(\infty)$ in particles a few atoms across and rapidly decreased as particle size increased (Figure 3.5). The particle size at which ΔT_C became negligible was found to vary between crystal structures; in bcc particles this size was 20 atoms (~ 2 nm), and in magnetite 50 atoms (~ 5 nm). ΔT_C was found to be insensitive to changes in the exchange energy between neighbouring atoms, showing that

crystal structure is the primary driver of the differences in T_C due to shape. All systems were fitted to the finite-size scaling law of *Fisher and Ferdinand* (1967) and a good fit was found in all cases. Very small particles, typically $d < 10$ -20 atoms, showed deviation away from finite-size scaling behaviour. Values of ν were found to lie in the range 0.46-0.55, which compare well to the analytical mean-field value of $\nu = 0.5$. No trend in the value of ν with relation to particle shape was found. A modified scaling law, derived from Ginzberg-Landau theory, accounted for the observed deviation from finite-size scaling in simple cubic and bcc particles; however, it was unsuccessful when applied to magnetite. This may be due to the complex crystal structure of magnetite which involves interactions over many layers of the unit cell, in contrast to the simpler sc and bcc ordering for which the modified scaling law was derived.

In Chapter 4 the Wien2k DFT package was used to calculate nearest neighbour exchange energies in magnetite and maghemite. Values for J_{AB} , J_{AA} and J_{BB} in magnetite have previously been estimated both experimentally (*Néel*, 1948; *Brockhouse and Watanabe*, 1963; *Bourdonnay et al.*, 1971) and numerically (*Uhl and Siberchicot*, 1995), but to my knowledge no numerical or experimental estimates of exchange energies in maghemite have ever been made. Due to the different approximations made by different methods for estimating J_{ij} , it is desirable to calculate both sets of exchange energies within a consistent framework. This framework consisted of spin polarised GGA+U calculations, in which the value of the Hubbard potential, U , was to be chosen based on the results of calculations on magnetite.

Exchange energies in magnetite were calculated using the least-squares method applied to the 18 unique spin configurations of a magnetite structure with the $Pmm2$ spacegroup and using values of $U = 2.0, 3.0$ and 3.8 eV; the latter value taken from previous Wien2k calculations on magnetite (*Bliem et al.*, 2014). The best fit values of J_{AA} and J_{BB} were found to vary little with changes in U , but the principle J_{AB} values was found to have a linear dependence on the value of U , with the interaction becoming more strongly antiferromagnetic as the value of U decreased. When $U = 3.8$ eV, best fit values of $J_{AB} = -2.47$ meV, $J_{AA} = -0.54$ meV and $J_{BB} = -0.16$ meV were found to be in reasonable agreement with previous experimental results (*Möglestue*, 1968; *Bourdonnay et al.*, 1971), particularly in the case of the principal J_{AB} interaction. However, the corresponding Curie temperature in a Monte Carlo model of magnetite was 660 K, nearly 200 K below the experimental value of T_C (*Pauthenet and Bochirol*, 1951). In contrast, the exchange energies obtained when a value of $U = 3$ eV was applied were $J_{AB} = -3.16$ meV, $J_{AA} = -0.93$ meV and $J_{BB} = -0.08$ meV and led to a Curie temperature of 840 K in good agreement with the experimental value of T_C . These new values may offer a small improvement to Monte Carlo simulations over the values obtained by *Uhl and Siberchicot* (1995).

The maghemite crystal structure contains fully ordered vacancies in the $4b$ Wyckoff positions (*Shmakov et al.*, 1995). This leads to a structure with the $P4_12_12$ spacegroup, which requires a $3 \times 1 \times 1$ supercell to describe (*Grau-Crespo et al.*, 2010). The presence of these vacancies resulted

in large forces on many of the atoms inside the maghemite cell. Resolving these forces through geometry optimisation lead to differences in the non-magnetic component of the total energy between the different spin configurations. As the least-squares method requires the non-magnetic energy to remain constant (or at least very similar) between different spin configurations, this led to the failure of the least squares method in predicting exchange energies in maghemite.

Monte Carlo simulations of partially oxidised magnetite-maghemite core-shell nanoparticles were made in Chapter 5. Magnetite-maghemite core-shell particles are widespread in the natural environment (*Prévot et al.*, 1981; *van Velzen and Dekkers*, 1999), yet previous studies on these systems on the nanoscale have been limited to their composition, structure and basic magnetic properties (*Santoyo Salazar et al.*, 2011; *Frison et al.*, 2013).

The effect of increasing oxidation on the Curie temperature and coercivity of core-shell particles in the size range 5.0-12.6 nm was investigated. The Curie temperature of a core-shell particle was found to increase non-linearly with fraction of maghemite. Due to the effects of finite-size scaling, the Curie temperatures of particles of different size had different values, but the relative change in T_C due to oxidation was found to be the same regardless of particle of size. A mechanism for the non-linear change in T_C with oxidation was proposed. The coercivity of core-shell particles was found to vary linearly with fraction of maghemite and is driven by the decrease in average exchange energy per atom as the particle oxidises.

6.1 Further work

The work in Chapter 3 predicts that the Curie temperature of very small magnetic nanoparticles has a strong dependence on shape. Experimental verification of this prediction would help towards confirming how these very fine particles behave. Due to the superparamagnetic nature of these particles such measurements would likely have to be conducted in the presence of a strong external magnetic field, and T_C recovered as the minimum of the derivative ($\frac{dM_S}{dT}$) of the resulting magnetisation curve (*Fabian et al.*, 2013). As preparation methods have only relatively recently become advanced enough to produce sub 10nm particles with narrow distributions of diameters, it seems reasonable to believe it will take another advance in such techniques to be able to have fine control over particle shapes at the sub 5 nm length scales. Our results suggest that the effect of shape on the Curie temperature is likely to be observable in larger particle sizes in materials such a magnetite, likely because the presence of oxygen reduces the density of magnetic atoms, as opposed to the elemental ferromagnets which suggests that magnetite may be a good candidate with which to perform such experiments.

Obtaining estimates of J_{ij} in maghemite remains an area of interest in rock magnetism. Doing so would allow for modern micromagnetic studies, such as those conducted using magnetite (*Nagy et al.*, 2017) to be conducted for maghemite. Depending on the results of such a study, the core-

shell modelling conducted here and by *Ge et al.* (2014) may then benefit from further work. From the perspective of DFT, the spin spiral method employed by *Uhl and Siberchicot* (1995) may offer an alternative method for estimating J_{ij} .

Titanomagnetite, which is common in oceanic basalts, is also an important naturally occurring magnetic material and is formed when some fraction of the Fe ions in the spinel lattice are replaced by Ti. To date, numerical studies have used exchange parameters estimated from the dependence of T_C on the composition of a sample within the titanomagnetite series (*Khakhalova et al.*, 2018) and estimates of J_{ij} would allow for more accurate numerical studies into the properties of titanomagnetite. The lack of vacancies in such a structure suggest that it may be possible to make J_{ij} estimations using the least-squares method.

The origin of the non-linear change in T_C with progressing oxidation in magnetite-maghemite core-shell nanoparticles has not been completely resolved in this thesis and further work to understand it would be beneficial. The effect of surface anisotropy has been neglected in the Monte Carlo simulations conducted here, but its magnitude is generally considered to be ~ 10 times greater than magnetocrystalline anisotropy. Spin canting has been observed on the surface of many nanoparticle systems and its effect on the behaviour of core-shell particles may be of interest. To my knowledge, experimental studies of magnetite-maghemite core-shell nanoparticles are yet to investigate the effect of oxidation on hysteresis and Curie temperature, and an experimental study into the effects studied here would help improve understanding of these systems.

Appendix A

Derivation of mean-field equations

The derivation presented here applies the mean-field approximation to finite systems of spins in three spatial dimensions; it is closely related to work conducted previously *Fabian et al.* (2015), but restricts the spin orientations and the applied field to lie in one direction. However, the final set of equations here feature a factor of S_i inside the Brillouin function which is not present in the former work. This discrepancy arises between (A.16) and (A.20), which is treated as a single step in the previous work, and so a full treatment is given here for clarity.

The Heisenberg Hamiltonian for a system of N magnetic spins considering exchange and external field h is given by *Stanley* (1987),

$$\mathcal{H} = -2 \sum_{\langle ij \rangle} J_{ij} S_i S_j - g \mu_B h \sum_{i=1}^N S_i, \quad (\text{A.1})$$

where S_i is the spin of site i , J_{ij} is the isotropic exchange energy ($J_{ij} = J_{ji}$) between sites i and j , $g \approx 2$ is the gyromagnetic ratio, μ_B is the Bohr magneton and h is an external field acting on each site. The sum over $\langle ij \rangle$ is over nearest neighbour pairs. The definition of the Heisenberg Hamiltonian here gives a positive value to ferromagnetic and a negative value to antiferromagnetic exchange energies. The sum of the first term is taken over each nearest neighbour pair of sites and may be re-written as,

$$\mathcal{H} = - \sum_{i=1}^N \sum_{j \in N_i} J_{ij} S_i S_j - g \mu_B h \sum_{i=1}^N S_i, \quad (\text{A.2})$$

where N_i is the set of nearest neighbour spins of site i .

The temporal fluctuation, δ_i of the i^{th} spin is defined as *Christensen and Moloney* (2005),

$$\delta_i = S_i - \langle S_i \rangle, \quad (\text{A.3})$$

where $\langle S_i \rangle$ is the average value or magnetisation of spin i . The Hamiltonian in terms of δ_i may be written as,

$$\mathcal{H} = - \sum_{i=1}^N \sum_{j \in N_i} J_{ij} (\delta_i \delta_j + \delta_i \langle S_j \rangle + \langle S_i \rangle \delta_j + \langle S_i \rangle \langle S_j \rangle) - g\mu_B h \sum_{i=1}^N S_i. \quad (\text{A.4})$$

The mean-field approximation is taken, in which correlations between fluctuations are neglected (i.e. $\langle \delta_i \delta_j \rangle = 0$). This gives the mean-field Hamiltonian,

$$\mathcal{H}_{\text{MF}} = - \sum_{i=1}^N \sum_{j \in N_i} J_{ij} (\delta_i \langle S_j \rangle + \langle S_i \rangle \delta_j + \langle S_i \rangle \langle S_j \rangle) - g\mu_B h \sum_{i=1}^N S_i. \quad (\text{A.5})$$

Substitution of equation (A.3), and summation over all sites allows simplification to,

$$\mathcal{H}_{\text{MF}} = \sum_{i=1}^N \sum_{j \in N_i} J_{ij} (\langle S_i \rangle \langle S_j \rangle - 2S_i \langle S_j \rangle) - g\mu_B h \sum_{i=1}^N S_i. \quad (\text{A.6})$$

In order to find the equilibrium state of the system, the minimum of the free energy must be found. The free energy, F is given in terms of the well known equation $F = -k_B T \ln Z$ where Z is the partition function. The partition function is given by the expression,

$$Z = \sum_{\{S_i\}} \exp \left(\frac{-\mathcal{H}}{k_B T} \right), \quad (\text{A.7})$$

where $\{S_i\}$ is the sum over all possible states of the system defined by $\mathcal{H}$. Substitution of (A.6) and the quantisation of angular momentum yields the following expression for the partition function,

$$Z = \exp \left(- \sum_{i=1}^N \sum_{j \in N_i} \frac{J_{ij} \langle S_i \rangle \langle S_j \rangle}{k_B T} \right) \prod_{i=1}^N \sum_{\sigma = -S_i}^{S_i} \exp(\xi_i \sigma), \quad (\text{A.8})$$

where,

$$\xi_i = \frac{\sum_{j \in N_i} 2J_{ij} \langle S_j \rangle + g\mu_B h}{k_B T}. \quad (\text{A.9})$$

Noting the geometric series summation, a final expression for Z is given by,

$$Z = \exp \left(- \sum_{i=1}^N \sum_{j \in N_i} \frac{J_{ij} \langle S_i \rangle \langle S_j \rangle}{k_B T} \right) \prod_{i=1}^N \frac{\sinh \left(\frac{2S_i+1}{2} \xi_i \right)}{\sinh \left(\frac{1}{2} \xi_i \right)}. \quad (\text{A.10})$$

The free energy can be calculated by direct substitution,

$$F = \sum_{i=1}^N \sum_{j \in N_i} J_{ij} \langle S_i \rangle \langle S_j \rangle - k_B T \sum_{i=1}^N \ln \frac{\sinh \left(\frac{2S_i+1}{2} \xi_i \right)}{\sinh \left(\frac{1}{2} \xi_i \right)} = F_1 - F_2. \quad (\text{A.11})$$

The equilibrium state of the system occurs when the derivative of free energy with respect to each magnetisation, $\frac{\partial F}{\partial \langle S_i \rangle} = 0$. The two terms of the free energy are considered separately,

$$F_1 = \sum_{i=1}^N \sum_{j \in N_i} J_{ij} \langle S_i \rangle \langle S_j \rangle, \quad (\text{A.12})$$

and

$$F_2 = k_B T \sum_{i=1}^N \ln \frac{\sinh\left(\frac{2S_i+1}{2}\xi_i\right)}{\sinh\left(\frac{1}{2}\xi_i\right)}. \quad (\text{A.13})$$

The partial derivative of F_1 yields,

$$\frac{\partial F_1}{\partial \langle S_i \rangle} = \sum_{j \in N_i} 2J_{ij} \langle S_j \rangle, \quad (\text{A.14})$$

where the factor of two arises from the sum over all sites. The case of F_2 requires a little more manipulation but finally obtains the expression,

$$\frac{\partial F_2}{\partial \langle S_i \rangle} = \sum_{j \in N_i} 2J_{ij} \left[\frac{2S_j+1}{2} \coth\left(\frac{2S_j+1}{2}\xi_j\right) - \frac{1}{2} \coth\left(\frac{1}{2}\xi_j\right) \right], \quad (\text{A.15})$$

which is related to the Brillouin function by,

$$\frac{\partial F_2}{\partial \langle S_i \rangle} = \sum_{j \in N_i} 2J_{ij} S_j B_{S_j}(S_j \xi_j), \quad (\text{A.16})$$

or equivalently,

$$\frac{\partial F_2}{\partial \langle S_i \rangle} = \sum_{j \in N_i} 2J_{ij} S_j B_{S_j} \left(S_j \frac{\sum_{k \in N_j} 2J_{jk} \langle S_k \rangle + g\mu_B h}{k_B T} \right). \quad (\text{A.17})$$

The sum over j is a summation over the nearest neighbours of site i , whilst the sum over k is a sum over the nearest neighbours of site j . A minimum of free energy is therefore found when,

$$\frac{\partial F}{\partial \langle S_i \rangle} = \sum_{j \in N_i} 2J_{ij} [\langle S_j \rangle - S_j B_{S_j}(S_j \xi_j)] = 0. \quad (\text{A.18})$$

Each term in the sum must equal zero to prevent solutions featuring the self interaction of spins, and so the solution to (A.18) reduces to N coupled equations,

$$\langle S_i \rangle = S_i B_{S_i} \left(S_i \frac{\sum_{j \in N_i} 2J_{ij} \langle S_j \rangle + g\mu_B h}{k_B T} \right). \quad (\text{A.19})$$

By defining the site normalised magnetisation $m_i = \frac{\langle S_i \rangle}{S_i}$, the final form of (A.19) is,

$$m_i = B_{S_i} \left(S_i \frac{\sum_{j \in N_i} 2J_{ij} S_j m_j + g\mu_B h}{k_B T} \right). \quad (\text{A.20})$$

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