Atomistic simulations of magnetic models with coupled translational and
spin degrees of freedom

by

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(Under the direction of David P. Landau)

Abstract

Using an atomistic model that treats translational and spin degrees of freedom on an equal
footing, we perform combined molecular and spin dynamics (MD-SD) and Monte Carlo (MC)
simulations to study the dynamic and static (thermodynamic) properties of body-centered
cubic (bcc) iron. The atomic interactions are modeled via an empirical many-body potential
while spin-spin interactions are established through a Heisenberg-like Hamiltonian with a
coordinate-dependent exchange interaction parameterized by first-principles calculations. In
MD-SD simulations, the numerical solutions to the coupled equations of motion were ob-
tained using an algorithm based on the second-order Suzuki-Trotter decomposition of the
exponential time evolution operator. By calculating the Fourier transforms of the space-
and time-displaced correlation functions, the characteristic frequencies and the linewidths of
the vibrational and magnetic excitation modes were determined. Comparison of the results
with that of the stand-alone molecular dynamics and spin dynamics simulations reveal that
the dynamic interplay between the phonons and magnons leads to a shift in the respective
frequency spectra and a decrease in the lifetimes. Moreover, in the presence of lattice vibra-
tions, additional longitudinal magnetic excitations were observed with the same frequencies
as the longitudinal phonons. A generic, phenomenological approach was developed for incorporating spin-orbit interactions into the MD-SD formalism. These interactions are modeled in terms of the local magnetic anisotropies that arise as the symmetry of the local crystal structure is broken due to phonons or crystallographic defects. Using canonical MD-SD simulations, we show that this novel extension overcomes the major shortcoming of the original method; namely, the inability to achieve the mutual thermalization of both the atomic and spin degrees of freedom via a heat bath coupled to the lattice subsystem. Using massively parallel replica-exchange Wang–Landau MC simulations, the magnetic phase transition in bcc iron was investigated with/without the impact of the phonons. The transition temperature as well as the amplitude of the peak in the specific heat curve is marginally affected by the lattice vibrations. However, the results were also found to be sensitive to the particular choice of the interatomic potential.

INDEX WORDS: molecular dynamics, spin dynamics, bcc iron, Suzuki-Trotter decomposition, phonon-magnon interactions, spin-orbit coupling, magnetocrystalline anisotropy, replica-exchange Wang–Landau sampling
Atomistic simulations of magnetic models with coupled translational and spin degrees of freedom

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Chapter 1

Introduction

Magnetism is one of the most fundamental physical properties of matter, and plays an increasingly important role in the technological advancements of the modern industrial world. Today, magnetic materials are ubiquitously used in all major disciplines of science and engineering, with applications as diverse as magnetic recording, electric power generation and transmission, magnetic resonance imaging (MRI), magnetocaloric refrigeration, telecommunication, magnetic levitation and transportation, spintronics etc.

Despite being one of the oldest natural phenomena known to mankind, the underlying principles behind the origin of magnetism have eluded scientists for centuries and are still far from being fully understood. The microscopic mechanisms responsible for the formation of atomic magnetic moments as well as their interactions are complex and subtle, and may vary across different classes of materials. For instance, in rare earth metals, the $4f$ electrons that primarily contribute to the atomic magnetic moments are strongly localized close to the atomic nuclei [1, 2], whereas in transition metals, $3d$ electrons are hybridized with $4s$ states, which allows them to exhibit behavior that is both localized and itinerant at the same time [3, 4, 5, 6]. In fact, this hybrid nature of the $3d$ electrons is the primary cause of strong ferromagnetic ordering at finite temperatures as observed in transition metals such as iron.
(Fe), cobalt (Co), and nickel (Ni). In these metals, the localization of 3d electrons is high enough to produce sizable atomic magnetic moments, yet low enough to provide overlap between the electronic wave functions at neighboring sites to generate strong interatomic exchange interactions \[6\]. As a result, unlike in the case rare earth metals, Fe, Co, and Ni have Curie temperatures that are well above the room temperature.

Our understanding of the metallic magnetism has been greatly enhanced over the past few decades due to the development of various computational approaches. Electronic structure calculations based on the density functional theory have provided information regarding the atomic-scale magnetic structure (i.e. magnetic moments, exchange energies etc.) with remarkable accuracy \[7, 8, 9, 10\]. However, despite the recent advancements, these first-principles based approaches are restricted to the calculation of ground state properties and are incapable of predicting the collective behavior of atomic magnetic moments at finite temperatures. Much of our current knowledge of the finite-temperature magnetism has been derived from atomistic simulations of classical spin models which treat the magnetic crystal as a system of interacting atomic magnetic moments on a rigid lattice (e.g. Ising model \[11\] and Heisenberg model \[12\]). In this regard, Monte Carlo (MC) simulations \[11, 13, 14\] have been extensively used for efficiently sampling the complex phase space associated with these simplified models and obtain reliable estimates of the thermodynamic properties.

An alternative approach of extracting information from classical spin models is to numerically solve the equations of motion governing the time evolution of the atomic spins. The so-called “spin dynamics (SD)” method has been successfully employed in the past few decades to investigate the dynamical behavior of spin systems with continuous degrees of freedom \[15, 16, 17, 18, 19\]. In contrast to MC methods, SD simulations initiated from equilibrium states drawn from the Canonical ensemble can directly reveal the elementary magnetic excitations (e.g. spin waves and solitons) that determine the equilibrium magnetic properties of the system at the corresponding temperature. By choosing exchange interaction
parameters determined from experiments or first principle calculations, one can construct realistic models of magnetic materials, where the obtained results pertaining to the collective excitations can be quantitatively compared to that of the inelastic neutron scattering experiments [20, 21, 22].

Recent, rapid advancements in SD simulations were largely due to the emergence of a novel class of symplectic integrators based on the Suzuki-Trotter decomposition of the exponential time evolution operator [23, 24, 25, 26]. These algorithms are known to be time reversible, and conserve phase-space volume exactly. In comparison to the conventional predictor-corrector integration schemes, decomposition methods are superior in terms of the numerical stability, accuracy as well as efficiency [24].

Despite being the de facto standard for modeling magnetic systems at finite temperatures, the validity of lattice-based spin systems in the context of real magnetic materials is highly debatable. These models inherently fail to capture the wide range of intricate phenomena that may occur at both microscopic and macroscopic level due to the coexistence of lattice vibrations (phonons) and spin waves (magnons). For instance, in transition metals and alloys, the atomic magnetic moments and the exchange interactions strongly depend on the local atomic environment [27, 28, 29], and hence, will change dynamically as the local crystal structure is distorted by the lattice vibrations [30]. On the other hand, magnetic interactions themselves play a pivotal role in maintaining the structural stability of such systems [31, 32]. For instance, the stabilization of body centered cubic (bcc) crystal structure in iron at room temperature has long conceived to be of magnetic origin, whereas in the absence of magnetism, it is expected to adopt the hexagonal closed packed (hcp) structure [33, 34]. Moreover, recent studies have revealed that in iron-based alloys, spin-lattice coupling significantly influences the thermal transport properties [35], defect evolution [36], and the equilibrium thermodynamic behavior [30], especially at elevated temperatures. All in all, any atomistic model designed to provide an accurate description of a magnetic transition
metal should, in principle, treat the dynamics of translational and spin degrees of freedom on an equal footing.

To the best of our knowledge, the first attempt to incorporate the dynamics of translational degrees of freedom into a classical spin model was made by Omelyan et al. [37] in the context of a simple model for Heisenberg ferrofluids. By taking the exchange interaction as a pairwise function of interatomic distance, they presented a dynamical simulation model that could be exploited via combined molecular and spin dynamics (MD-SD) simulations. For integrating the coupled equations of motion, Omelyan et al. devised a novel algorithm based on the Suzuki-Trotter decomposition of the complete time evolution operator which includes both translational and spin degrees of freedom. Using an empirical many-body potential and an exchange interaction parameterized by first principles calculations, Ma et al. [38] further extended the idea of coupled molecular and spin dynamics into a more realistic model for the treatment of bcc iron. The computational framework along with the parameterization developed by Ma et al. [38] has ever since been successfully adopted to investigate various phenomena in bcc iron such as magneto-volume effects [39], vacancy formation and migration [40, 41], and external magnetic field effects [42]. Moreover, an adaptation of the method has been recently applied to Co nanosystems with large shape anisotropies [43].

The focus of this dissertation is threefold. First, we utilize the MD-SD approach and the parameterization developed by Ma et al. to investigate phonon-magnon interactions in bcc iron. Specifically, our intent is to understand the mutual influence of the phonons and magnons on their respective frequency spectra and lifetimes at finite temperatures. To achieve this, we simultaneously measure the space- and time-displaced correlation functions associated with the respective phase variables and obtain their Fourier transforms. The resultant quantity, also known as the dynamic structure factor [44, 45, 17], directly conveys information regarding the frequencies and lifetimes of the excitation modes. Second, we propose a novel extension to the MD-SD framework for modeling spin-orbit interactions. The
foundation of this method lies in the incorporation of the local magnetic anisotropies that arise as a consequence of the lattice symmetry breaking due to phonons or crystallographic defects. This novel extension enables the simultaneous thermalization of both translational and spin degrees of freedom via a thermostat coupled to the lattice subsystem, a task that cannot be achieved with the original MD-SD formulation. Third, we apply the the recently introduced massively parallel replica-exchange Wang–Landau Monte Carlo approach [46, 47, 48, 49] to explore the magnetic phase transition in bcc iron with/without the influence of the lattice vibrations.

The remainder of this dissertation is organized as follows: In Chapter 2, we provide brief introductions to the fundamental concepts of statistical mechanics and classical spin dynamics, followed by a description of the MD-SD formalism and the parameterization that we adopt for modeling bcc iron. Chapter 3 describes the simulation algorithms and techniques, including Monte Carlo methods (Metropolis and Wang-Landau approaches), the time integration algorithm used in MD-SD simulations, the parallelization scheme for spin dynamics, thermostat algorithms for controlling temperature, and methods of characterizing collective excitations. In Chapter 4, we present and discuss our simulation results on phonon-magnon interactions. Chapter 5 will introduce our novel extension to MD-SD for modeling spin-orbit interactions, followed by canonical simulation results that prove the effectiveness of the model. In Chapter 6, we show our results of replica-exchange Wang–Landau simulations. Finally, in chapter 7, we summarize our findings and provide concluding remarks.
Chapter 2

Background

2.1 Fundamental concepts in classical statistical mechanics

A typical macroscopic system that one observes through experiments usually consists of an enormously large number of interacting atoms and molecules, with positions and momenta that continuously evolve according to their equations of motion. However, if in thermal equilibrium, the thermodynamic state (i.e. macrostate) of the system can be solely specified in terms of a handful of physically observable parameters such as the number of particles $N$, volume of the system $V$, temperature $T$ etc. Statistical mechanics establishes the connection between the microscopic level details concerning the dynamical evolution of the individual particles and the overall thermodynamic behavior of the system as depicted by these macroscopic observables [50, 51].

Let $\{q_i\}$ and $\{p_i\}$ be the generalized coordinates and the conjugate momenta for a monatomic system of $N$ atoms that are physically distributed in three dimensional space. The $6N$-dimensional hyperspace constructed from these $6N$ variables is called the “phase space” of the system. A particular point $\Gamma$ in this phase space as specified by a particular
phase vector $\mathbf{x} = (\{q_i\}, \{p_i\})$ is called a “microstate”. Given the Hamiltonian $\mathcal{H}(\mathbf{x})$, the time evolution of the system is governed by the canonical equations of motion [51]

$$
\dot{q}_j = -\frac{\partial \mathcal{H}}{\partial p_i}, \quad \dot{p}_j = \frac{\partial \mathcal{H}}{\partial q_i}. \tag{2.1}
$$

Eqs. (2.1) determine the trajectory of the phase vector $\mathbf{x}$ in time. Let $A(\mathbf{x}(t))$ be the instantaneous value of some physically observable quantity $A$. The experimentally observed value for $A$ is the time average of $A(\mathbf{x}(t))$ taken over a long period of time:

$$
A_{\text{obs}} = \lim_{t_{\text{obs}} \to \infty} \frac{1}{t_{\text{obs}}} \int_0^{t_{\text{obs}}} A(\mathbf{x}(t)) dt. \tag{2.2}
$$

In statistical mechanics, one seeks to replace the time average in (2.2) by an average over an ensemble of systems at a particular instance in time. Here, an “ensemble” refers to an infinitely large number of “virtual copies” of the system characterized by the same macrostate, but distributed among different microstates according to a certain probability density $\rho_{\text{ens}}(\mathbf{x})$. With time, the individual members of the ensemble will move along their own phase space trajectories. For a system in equilibrium, $\rho_{\text{ens}}(\mathbf{x})$ represents a stationary probability distribution, determined by a chosen fixed set of thermodynamic variables. Each ensemble can be uniquely defined in terms of three such variables. For instance, in the microcanonical ($NVE$) ensemble, the fixed variables are $N$ (number of particles), $V$ (volume), and $E$ (energy), whereas for the canonical ($NVT$) ensemble, they are $N$, $V$, and $T$ (temperature). According to the ergodic hypothesis, the time average of a thermodynamic quantity given by Eq. (2.2) is identical to the average taken over all the members of the ensemble at a particular instance in time [52, 51], i.e

$$
A_{\text{obs}} = \langle A(\mathbf{x}) \rangle_{\text{ens}} = \sum_{\mathbf{x}} A(\mathbf{x}) \rho_{\text{ens}}(\mathbf{x}). \tag{2.3}
$$
(Note that in principle, for systems with continuous degrees of freedom, the summation in Eq. (2.3) should be replaced by the appropriate integral. For the ongoing discussion, we will continue to use the summation due to simplicity.)

In the formulation of statistical mechanics, it is customary to replace the probability density $\rho_{\text{ens}}(x)$ with an unnormalized weight function $w_{\text{ens}}(x)$ such that $w_{\text{ens}}(x) \propto \rho_{\text{ens}}(x)$. Ensemble average (2.3) can be rewritten in terms of these weight functions as

$$\langle A(x) \rangle_{\text{ens}} = \frac{1}{Q_{\text{ens}}} \sum_x A(x) w_{\text{ens}}(x),$$

(2.4)

where the normalization factor $Q_{\text{ens}} = \sum_x w_{\text{ens}}(x)$ is called the partition function. In principle, the partition function incorporates all the essential information regarding the thermodynamic behavior of the system pertaining to the given ensemble. To establish the link between the microscopic details and the thermodynamic macrostate, we define a thermodynamic potential as [52]

$$\Psi_{\text{ens}} = -\ln Q_{\text{ens}}$$

(2.5)

This function has a minimum value at the thermodynamic equilibrium of the corresponding ensemble.

**2.1.1 Microcanonical ensemble**

In the microcanonical, or $NVE$ ensemble, the accessible microstates are restricted to a constant energy surface in the phase space given by

$$\mathcal{H}(x) = E.$$ 

(2.6)

We assume that all microstates with the same energy $E$ occur with equal probability. Thus, the probability density $\rho_{NVE}(x)$ is proportional to $\delta(\mathcal{H}(x) - E)$, which yields the microcanon-
ical partition function

\[ Q_{\text{NE}} = \sum_{x} \delta(\mathcal{H}(x) - E). \]  

(2.7)

The appropriate thermodynamic potential based on the definition given in Eq. (2.5) is

\[ -S/k_B = -\ln Q_{\text{NE}}, \]  

(2.8)

where \( S \) is the microcanonical entropy.

For classical systems, Hamilton’s equations (2.1) (in other words, Newton’s laws of motion) conserve energy, thus providing a natural means of generating a sequence of microstates sampled from this ensemble. This is the foundation for the famous molecular dynamics (MD) simulation method [53, 54, 52]. In the absence of external forces, Hamilton’s equations also conserve total linear momentum \( P \). Thus, in principle, MD simulations sample a subset of the microcanonical ensemble, namely \( \text{NVEP} \) ensemble [52].

### 2.1.2 Canonical ensemble

From a practical point of view, the microcanonical ensemble does not correspond to a naturally occurring process in real physical systems. Since no real physical system is completely isolated, exchange of energy between the system and the outside environment occurs, leading to fluctuations in energy. Even in an experimental setting, it is impracticable to control and maintain the total energy of the system at a fixed value. A better alternative is to define an ensemble where the constraint on fixed energy is replaced by fixed temperature \( T \). The so-called canonical, or \( \text{NVT} \) ensemble provides the basis for describing the thermodynamics of systems in contact with external heat reservoirs.

In the canonical ensemble, the weights are given by the Boltzmann distribution

\[ \rho_{\text{NVE}}(x) \propto e^{-\beta \mathcal{H}(x)}, \]  

(2.9)
and the partition function takes the form

\[ Q_{NVT} = Z = \sum_x e^{-\beta H(x)}, \]  

(2.10)

where \( \beta = 1/k_B T \), with \( k_B \) being the Boltzmann constant. The appropriate thermodynamic potential is the Helmholtz free energy

\[ F/k_B T = -\ln Z. \]  

(2.11)

The canonical ensemble averages are given by

\[ \langle A \rangle_{NVT} = \frac{1}{Z} \sum_x A(x) e^{-\beta H(x)}. \]  

(2.12)

For instance, the ensemble average of energy \( \langle H \rangle_{NVT} \), also known as the internal energy \( U \), is

\[ U = \langle H \rangle_{NVT} = \frac{1}{Z} \sum_x H(x) e^{-\beta H(x)}. \]  

(2.13)

From Eq. (2.10) we identify that \( U \) can also be written in terms of the derivative of the partition function:

\[ U = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = -\frac{\partial \ln Z}{\partial \beta}. \]  

(2.14)

Then, the heat capacity at constant volume takes the form

\[ C_V = \left( \frac{\partial U}{\partial T} \right)_V = -\frac{1}{k_B T^2} \frac{\partial^2 \ln Z}{\partial \beta^2}. \]  

(2.15)

In addition to the thermal averages of macroscopic observables, statistical mechanics can also characterize their fluctuations about the mean values. For instance, fluctuations in
energy are described by

\[
\left\langle (\mathcal{H} - \langle \mathcal{H} \rangle_{NVT})^2 \right\rangle_{NVT} = \langle \mathcal{H}^2 \rangle_{NVT} - \langle \mathcal{H} \rangle_{NVT}^2,
\]  

(2.16)

with \( \langle \mathcal{H} \rangle_{NVT} \) given by Eq. (2.13) and \( \langle \mathcal{H}^2 \rangle_{NVT} \) given by

\[
\langle \mathcal{H}^2 \rangle_{NVT} = \frac{1}{Z} \sum_x \mathcal{H}(x)^2 e^{-\beta \mathcal{H}(x)}.
\]  

(2.17)

From Eq. (2.15) it follows that

\[
k_B T^2 C_V = \langle \mathcal{H}^2 \rangle_{NVT} - \langle \mathcal{H} \rangle_{NVT}^2.
\]  

(2.18)

Since the expectation values \( \langle \mathcal{H} \rangle_{NVT} \) and \( \langle \mathcal{H}^2 \rangle_{NVT} \) can be readily estimated from the time series of Monte Carlo and molecular dynamics simulations, Eq. (2.18) provides a convenient way of estimating the heat capacity from simulations.

2.2 Theory of classical spin dynamics

2.2.1 Classical Heisenberg model

The foundation of the classical theory of magnetism lies in conceptualizing a magnetic crystal as a collection of individual atomic magnetic moments with fixed lengths [5, 12, 55]. In the presence of an external magnetic field, these magnetic moments may align along the direction of the field, resulting in a non-zero net magnetic moment. If the magnetic moments are non-interacting, in the absence of the field the moments are expected to be thermally disordered at any temperature, yielding a zero net magnetic moment. However, there are materials (i.e. ferromagnets) that exhibit nonvanishing magnetic moment or “spontaneous magnetization” below a certain critical temperature \( T_c \), even in the absence of an external
field. In another class of materials called antiferromagnets, the individual magnetic moments add up to give zero net magnetic moment, but the neighboring moments favor antiparallel alignment, resulting in a far from random spatial ordering of the moments. Such ferro- and antiferromagnetic ordering of spins can only be explained through the existence of correlations or mutual interactions between the atomic magnetic moments.

At a first glance, one may speculate that the magnetic ordering arise directly from magnetic dipole-dipole interactions. However, for a typical magnetic solid, the estimated values of these dipole-dipole interactions are of the order of $10^{-4}$ eV, and are clearly insufficient to produce the observed spontaneous ordering of the moments [12]. As it turns out, by far, the dominant source of magnetic interactions in solids is electrostatic in nature, driven by the Pauli exclusion principle which requires electrostatic energy between two electrons to depend on the relative orientation of their spins [5, 12]. The energy difference associated with this interaction, the “exchange energy”, can be represented by a simple quantum mechanical spin Hamiltonian of the form

$$\hat{H} = -J \hat{s}_1 \cdot \hat{s}_2,$$

where $\hat{s}_1$ and $\hat{s}_2$ are the electron spin operators, and $J$ is the exchange interaction, which is related to the overlap of the wave functions of the two electrons.

For magnetic ions with many electrons, one can generalize the electron spin-spin interaction in Eq. (2.19) to an effective interaction between the total spin angular momentum operators associated with the two ions. Moreover, for many systems, treating these spin angular momentum operators as classical spin vectors has found to be a very good approximation [55]. Considering these arguments, we sum over the exchange interactions between all ion pairs in the crystal to obtain the effective spin Hamiltonian (i.e. classical Heisenberg model)

$$\mathcal{H} = - \sum_{i<j} J_{ij} \textbf{S}_i \cdot \textbf{S}_j,$$
where $S_i$ is a three-dimensional vector associated with the $i$th lattice site, which represents the effective total spin of the $i$th ion. Spins have fixed magnitudes $|S_i|$, which are typically set to unity. The Hamiltonian favors parallel spins (ferromagnetic interaction) if $J > 0$ and anti-parallel spins (antiferromagnetic interaction) if $J < 0$. Although the summation in Eq. (2.20) is over all pairs of sites, for many systems, the exchange coupling tends to decrease rapidly with the increasing separation distance. Thus in practical applications, it is customary to limit the interactions to nearest neighbor sites.

Although Eq. (2.20) may appear as a crude approximation to the complex quantum mechanical origin of the magnetic interaction, it provides a surprisingly reasonable description of the magnetic phase transition in many materials. Nevertheless, extracting information even from the Heisenberg model is a non-trivial task which requires state-of-the-art computational methods and resources.

### 2.2.2 Equation of motion

Unlike its discrete spin counterpart the Ising model, Heisenberg model has true dynamics described by a classical equation of motion. Various methods of deriving this equation can be found in the literature, ranging from generalized Poisson brackets methods [56], to adopting the classical equation of motion for the undamped magnetization field [57, 58]. Here, we employ a quantum mechanical approach based on the Heisenberg picture, and take the classical limit of the end result to obtain the desired classical equation. According to the Heisenberg equation of motion, the time evolution of the spin operator $\hat{S}_i$ follows

$$\frac{d\hat{S}_i}{dt} = -\frac{i}{\hbar} [\hat{S}_i, \hat{H}].$$  \hspace{1cm} (2.21)
Using the quantum mechanical equivalent of Eq. (2.20): \[ \hat{H} = -\frac{1}{2} \sum_j k J_{jk} \hat{\mathbf{S}}_j \cdot \hat{\mathbf{S}}_k, \]
we evaluate the \( x \)-component of the commutator in Eq. (2.21) as

\[
\left[ \hat{S}_{ix}, -\frac{1}{2} \sum_{j,k} J_{jk} \hat{\mathbf{S}}_j \cdot \hat{\mathbf{S}}_k \right]
= \left[ \hat{S}_{ix}, -\frac{1}{2} \sum_{j,k} J_{jk} \left( \hat{S}_{jx} \hat{S}_{kx} + \hat{S}_{jy} \hat{S}_{ky} + \hat{S}_{jz} \hat{S}_{kz} \right) \right]
= -\frac{1}{2} \sum_{j,k} J_{jk} \left( \left[ \hat{S}_{ix}, \hat{S}_{jx} \right] \hat{S}_{kx} + \hat{S}_{jx} \left[ \hat{S}_{ix}, \hat{S}_{kx} \right] - \frac{1}{2} \sum_{j,k} J_{jk} \left[ \hat{S}_{ix}, \hat{S}_{jy} \right] \hat{S}_{ky} + \hat{S}_{jy} \left[ \hat{S}_{ix}, \hat{S}_{ky} \right] \right)
= -\frac{1}{2} \sum_{j,k} J_{jk} \left( \left[ \hat{S}_{ix}, \hat{S}_{jz} \right] \hat{S}_{kz} + \hat{S}_{jz} \left[ \hat{S}_{ix}, \hat{S}_{kz} \right] \right) \quad (2.22)

Using the cyclic commutation relations \( \left[ \hat{S}_{j\alpha}, \hat{S}_{k\beta} \right] = i\delta_{jk} \hat{S}_{j\gamma} \) and \( \left[ \hat{S}_{j\alpha}, \hat{S}_{k\alpha} \right] = 0 \) for \( \alpha, \beta, \gamma = x, y, z \), we obtain

\[
\left[ \hat{S}_{ix}, -\frac{1}{2} \sum_{j,k} J_{jk} \hat{\mathbf{S}}_j \cdot \hat{\mathbf{S}}_k \right]
= 0 - \frac{1}{2} \sum_{j,k} J_{jk} \left( \left[ i\delta_{ij} \hat{S}_{iz} \right] \hat{S}_{ky} + \hat{S}_{jy} \left[ i\delta_{ik} \hat{S}_{iz} \right] \right) - \frac{1}{2} \sum_{j,k} J_{jk} \left( \left[ -i\delta_{ij} \hat{S}_{iy} \right] \hat{S}_{kz} + \hat{S}_{jz} \left[ -i\delta_{ik} \hat{S}_{iy} \right] \right)
= -\frac{i}{2} \sum_{k(k\neq i)} J_{ik} \hat{S}_{iz} \hat{S}_{ky} - \frac{i}{2} \sum_{j(j\neq i)} J_{ji} \hat{S}_{jy} \hat{S}_{iz} + \frac{i}{2} \sum_{k(k\neq i)} J_{ik} \hat{S}_{iy} \hat{S}_{kz} + \frac{i}{2} \sum_{j(j\neq i)} J_{ji} \hat{S}_{jz} \hat{S}_{iy} \quad (2.23)

Changing variable \( k \to j \) and using \( J_{ji} = J_{ij} \), we get

\[
\left[ \hat{S}_{ix}, -\frac{1}{2} \sum_{j,k} J_{jk} \hat{\mathbf{S}}_j \cdot \hat{\mathbf{S}}_k \right] = i \sum_{j(j\neq i)} J_{ij} \left( \hat{S}_{jz} \hat{S}_{iy} - \hat{S}_{jy} \hat{S}_{iz} \right)
= i \left( \hat{S}_i \times \hat{H}^{\text{eff}}_i \right)_x, \quad (2.24)
\]
where $\hat{H}_i^{\text{eff}}$ is the effective field acting on the $i$th spin, given by

$$\hat{H}_i^{\text{eff}} = \sum_{j (j \neq i)} J_{ij} \hat{S}_j.$$ \hspace{1cm} (2.25)

Combining the equations (2.24) and Eq. (2.21), we obtain

$$\frac{d\hat{S}_i}{dt} = \frac{1}{\hbar} \hat{S}_i \times \hat{H}_i^{\text{eff}}.$$ \hspace{1cm} (2.26)

Now, we let the spin lengths to go to infinity and normalize them to a finite constant value (say, unity) to yield the classical equation of motion

$$\frac{dS_i}{dt} = \frac{1}{\hbar} S_i \times H_i^{\text{eff}},$$ \hspace{1cm} (2.27)

where $H_i^{\text{eff}} = \sum_{j (j \neq i)} J_{ij} S_j$. Often in spin dynamics simulations, it is customary to absorb $\hbar$ into the definition of $H_i^{\text{eff}}$ and perform calculations in reduced units. Note that the effective field $H_i^{\text{eff}}$ can be expressed in a more general form as the negative gradient of the Hamiltonian with respect to $S_i$, i.e. $H_i^{\text{eff}} = -\nabla_{S_i} \mathcal{H}$. In fact, the applicability of Eq. (2.27) is not limited to the Heisenberg exchange Hamiltonian (2.20), but is equally valid for any generalized Hamiltonian involving spins, with the appropriate effective field defined by $H_i^{\text{eff}} = -\nabla_{S_i} \mathcal{H}$.

In essence, Eq. (2.27) describes a rotation of the spin vector $S_i$ around the effective field $H_i^{\text{eff}}$, while keeping the length of the spin $|S_i|$ conserved. To show this, we consider the time evolution of the spin within a small time interval $\Delta t$, which follows directly from Eq. (2.27) as

$$S_i(t + \Delta t) = S_i(t) + \frac{1}{\hbar} S_i(t) \times H_i^{\text{eff}}(t) \Delta t.$$ \hspace{1cm} (2.28)
The magnitude of the spin vector $S_i$ at time $t + \Delta t$ is given by

$$|S_i(t + \Delta t)|^2 = S_i(t + \Delta t) \cdot S_i(t + \Delta t)$$

$$= |S_i(t)|^2 + \frac{2}{\hbar} S_i(t) \cdot (S_i(t) \times H_{\text{eff}}^i(t)) \Delta t + \frac{1}{\hbar^2} |S_i(t) \times H_{\text{eff}}^i(t)|^2 (\Delta t)^2 \quad (2.29)$$

Note that the second term vanishes since $S_i \cdot (S_i \times H_{\text{eff}}^i) = H_{\text{eff}}^i \cdot (S_i \times S_i) = 0$. In the limit $\Delta t \to 0$, the third term also vanishes, yielding

$$|S_i(t + \Delta t)|^2 = |S_i(t)|^2, \quad (2.30)$$

which explicitly proves the conservation of the spin length.

Let $\Delta S_i = S_i(t + \Delta t) - S_i(t)$. Then, from Eq. (2.28) it follows that

$$|\Delta S_i| = \frac{1}{\hbar} |S_i(t) \times H_{\text{eff}}^i(t)| \Delta t = \frac{1}{\hbar} |S_i(t)| |H_{\text{eff}}^i(t)| \sin \theta \Delta t, \quad (2.31)$$

where $\theta$ denotes the angle between $S_i(t)$ and $H_{\text{eff}}^i(t)$ (See Fig. 2.1). Since the vector $\Delta S_i(t)$ is perpendicular to $S_i(t)$, during the time interval $\Delta t$, the tip of the vector $S_i$ rotates around $H_{\text{eff}}^i$ by an angle

$$\Delta \phi = \frac{|\Delta S_i|}{|S_i(t)| \sin \theta} = \frac{1}{\hbar} H_{\text{eff}}^i(t) \Delta t. \quad (2.32)$$
2.3 Combined molecular and spin dynamics (MD-SD) approach

2.3.1 A generalized Hamiltonian for coupled spin-lattice systems

In the conventional molecular dynamics (MD) method [53, 52, 54], the total potential energy of a classical system of $N$ interacting atoms is considered to be a function of the atomic coordinates $\{r_i\}$, i.e. $U = U(\{r_i\})$. The functional form and the parameterization of $U$ depends on the particular system under investigation, and a substantial amount of work has been devoted to the construction of appropriate interatomic potentials for physical systems of interest. Combining $U$ with an explicit kinetic energy term, one can write the complete classical Hamiltonian of the system as

$$ \mathcal{H} = \sum_{i=1}^{N} \frac{m v_i^2}{2} + U(\{r_i\}), $$  \hspace{1cm} \text{(2.33)}

where $m$ the mass of an atom, and $\{v_i\}$ are the velocities.
The combined molecular and spin dynamics (MD-SD) method is essentially a reformulation of the MD approach, in which the effective spin angular momenta of the atoms \{S_i\} are incorporated into the Hamiltonian (2.33) and treated as explicit phase variables. The most intuitive way to accomplish this is to replace \( U(\{r_i\}) \) with a unified interaction potential \( U_{\text{un}}(\{r_i\}, \{S_i\}) \) which explicitly depends on both the atomic coordinates \{r_i\} and the spins \{S_i\}. However, the theoretical framework for deriving such a unified classical potential has not been established yet. Therefore, we adopt a semiempirical approximation and write \( U_{\text{un}}(\{r_i\}, \{S_i\}) \) as the sum of a non-magnetic scalar potential and a Heisenberg-like spin Hamiltonian, i.e

\[
U_{\text{un}}(\{r_i\}, \{S_i\}) \approx U_{\text{non-mag}}(\{r_i\}) - \sum_{i<j} J_{ij}(\{r_k\}) S_i \cdot S_j,
\]  

(2.34)

where \( U_{\text{non-mag}} \) represents the spin-independent scalar interaction between the atoms, and \( J_{ij}(\{r_k\}) \) is the coordinate-dependent exchange interaction. Finally, by explicitly incorporating kinetic energy, we write the complete Hamiltonian of our coupled spin-lattice system as

\[
\mathcal{H} = \sum_{i=1}^{N} \frac{m v_i^2}{2} + U_{\text{non-mag}}(\{r_i\}) - \sum_{i<j} J_{ij}(\{r_k\}) S_i \cdot S_j.
\]  

(2.35)

With \( U(\{r_i\}), J_{ij}(\{r_k\}) \), and the spin lengths chosen appropriately, one can readily adopt this model to any magnetic material in which the spin interactions can be modeled classically.

2.3.2 Equations of motion

A coupled spin-lattice system governed by the Hamiltonian (2.35) has true dynamics as described by three classical equations of motion.
The equations governing the time evolution of the positions and the velocities follow directly from the Hamilton equations as

\[
\begin{align*}
\frac{dr_i}{dt} &= v_i \\
\frac{dv_i}{dt} &= f_i/m
\end{align*}
\tag{2.36a, 2.36b}
\]

where \( f_i = -\nabla r_i \mathcal{H} \) is the force acting on the \( i \)th atom.

As shown in section 2.2.2, the precessional motion of the spins is described by the familiar spin dynamics equation

\[
\frac{dS_i}{dt} = \frac{1}{\hbar} S_i \times H^\text{eff}_i,
\tag{2.37}
\]

where \( H^\text{eff}_i = -\nabla S_i \mathcal{H} \) is the effective field.

The goal of the MD-SD approach is to numerically solve the above equations of motion starting from a given initial configuration, and obtain the trajectories of both the atomic and spin degrees of freedom. The specific details of the numerical methods used in solving the equations are discussed in section 3.2.

### 2.3.3 Global parameters for quantifying the magnetic state of the system

In this section, we introduce two global parameters that can quantitatively characterize the collinearity of the spin configuration.

**Spin temperature**

In the MD-SD formalism, one can perceive translational degrees of freedom (i.e. atomic positions and velocities) and magnetic degrees of freedom (i.e. spins) as constituents of two coupled subsystems, which will hereafter be referred to as the “lattice subsystem” and the
“spin subsystem”, respectively. The instantaneous temperature associated with the lattice subsystem can be readily measured via the familiar average kinetic energy expression:

$$T_L = \frac{2}{3k_B} \sum_{i=1}^{N} \frac{1}{2} m v_i^2. \quad (2.38)$$

Since, by definition, spin degrees of freedom are not paired with any conjugate momenta, a conceptually similar expression does not exist for measuring the temperature of the spin subsystem. However, starting from the microcanonical definition of the temperature, Nurdin et al. [59] recently developed a formula for quantifying the temperature of a spin ensemble, which can be entirely expressed in terms of its dynamic state variables as

$$T_S = \frac{\sum_i |S_i \times \nabla S_i H|^2}{k_B \sum_i (S_i \times \nabla S_i) \cdot (S_i \times \nabla S_i) H}. \quad (2.39)$$

In the absence of any nonlinear terms in the Hamiltonian with respect to spin variables \(\{S_i\}\), the above formula reduces to

$$T_S = \frac{\sum_i |S_i \times H^\text{eff}_i|^2}{2k_B \sum_i S_i \cdot H^\text{eff}_i}. \quad (2.40)$$

By solving the Langevin spin dynamics equation and applying the fluctuation-dissipation theorem [60], Ma et al. [61] independently arrived at the same equation (2.40) in the context of a canonical spin ensemble.

**Magnetization**

The net magnetization of the system is given by the sum of individual atomic magnetic moments:

$$M = \sum_{i=1}^{N} \mu_i, \quad (2.41)$$
with the atomic moments \( \{\mu_i\} \) defined in terms of the effective spins \( \{S_i\} \) via the relationship [55, 5]

\[
\mu_i = g \mu_B S_i, \tag{2.42}
\]

where \( \mu_B \) is the Bohr magneton, and \( g \) is the electron \( g \)-factor.

Due to the rotational symmetry of the isotropic Heisenberg Hamiltonian, the magnetization is conserved in conventional SD. Since the introduction of lattice vibrations does not break this symmetry, the magnetization still remains a conserved quantity in MD-SD if constant spin lengths are enforced (Details will follow in section 3.9).

Another consequence of the isotropic nature of the spin Hamiltonian is that the Cartesian components of the magnetization vector are equivalent. Thus, the magnitude of the magnetization \( M = \sqrt{M_x^2 + M_y^2 + M_z^2} \) alone provides a quantitative measure of the collinearity of the spin subsystem.

## 2.4 Parameterizing the MD-SD Hamiltonian for bcc iron

In this section, we discuss the parameterization of different components of the MD-SD Hamiltonian (2.35) for modeling bcc iron.

### 2.4.1 Non-magnetic scalar potential

In the Hamiltonian (2.35), the scalar potential \( U_{\text{non-mag}}(\{r_i\}) \) represents the non-magnetic contribution to the total potential energy. Due to the unavailability of interaction potentials that specifically exclude magnetic contributions, we construct \( U_{\text{non-mag}}(\{r_i\}) \) as

\[
U_{\text{non-mag}}(\{r_i\}) = U_{\text{EAM}}(\{r_i\}) - E_{\text{ground}}^{\text{spin}}, \tag{2.43}
\]
where $U_{EAM}$ represents a conventional interatomic potentials for bcc iron, and $E_{\text{spin}}^{\text{ground}} = - \sum_{i<j} J_{ij}(\{r_k\})|S_i||S_j|$ is the energy contribution from a collinear spin state, which we subtract out to eliminate the magnetic interaction energy implicitly contained in $U_{EAM}$. With the chosen form of $U_{\text{non-mag}}$, the Hamiltonian (2.35) provides the same energy as $U_{EAM}$ for the ferromagnetic ground state at 0 K.

As for $U_{EAM}$, we choose two well-established many-body potentials based on the embedded atom formalism, which will be discussed in detail in the following sections.

**Embedded atom formalism**

In molecular dynamics, arguably the most widely used models for interatomic potentials are the simple pairwise representations (e.g. Lennard Jones, Morse) [53, 52]. Although the use of pair potentials is justifiable for rare gases where the electron clouds are localized close to the atoms [53], they are inadequate for modeling metallic systems in which the valence electrons are delocalized and shared among the atoms. In this regard, the embedded atom method (EAM) [62, 63] presents an effective way of characterizing the many-body nature of the forces experienced by the individual metal ion cores immersed in this complex crystalline environment.

EAM potentials consist of two parts: A pairwise component which describes the repulsive interaction between the positively charged ion cores, and an attractive interaction which represents the energy associated with “embedding” the ion cores in the “sea” of valence electrons produced by the neighboring atoms. The general functional form of EAM potentials is given by [63]

$$U_{EAM} = \sum_{i=1}^{N} F[\rho_i] + \frac{1}{2} \sum_{i<j} V(r_{ij}), \quad (2.44)$$
where \( r_{ij} = |\mathbf{r}_i - \mathbf{r}_j| \), and the “electron density” \( \rho_i \) is constructed as the sum of pairwise density radial functions \( f(r_{ij}) \), i.e.

\[
\rho_i = \sum_{j=1}^{N} f(r_{ij}).
\]  

(2.45)

The introduction of the many-body interaction term leads to substantial improvements in the mechanical properties of the system, especially elastic constants and vacancy formation energy, which cannot be characterized properly via pairwise interactions [53]. EAM potentials are parameterized by fitting the chosen functional form to a list material properties obtained from experiments or first-principles calculations. The list of material properties typically consists of lattice constants, cohesive energy, elastic constants, vacancy and interstitial formation energies etc.

**Finnis-Sinclair potential**

The Finnis-Sinclair (FS) model [64] is one of the oldest, and perhaps the most commonly used class of EAM potentials for bcc metals. In the FS formalism, the embedding functional \( F[\rho] \) takes a simple analytical form

\[
F[\rho] = -A\sqrt{\rho},
\]  

(2.46)

which is motivated by the tight-binding theory in the second-moment approximation to the electron density of states [65].

In the original formulation of the FS potential [64], the pairwise functions \( v(r) \) and \( f(r) \) are given by

\[
v(r) = (r - c)^2(c_0 + c_1 r + c_2 r^2)\Theta(c - r),
\]  

(2.47)
and
\[ f(r) = (r - d)^2 + \frac{\beta}{d}(r - d)^3 \Theta(d - r), \] 
respectively, where \( \Theta(x) \) is the Heaviside step function. The optimal parameter set for bcc iron is given in Table 2.1.

Despite its simple empirical form and the short cut-off distance, FS potential can reproduce bulk material properties such as ground state energy, bulk moduli and elastic constants to a reasonable accuracy [66]. However, as the repulsive part of potential is too “soft”, FS potential tends to produce nonphysical results for disordered atomic configurations with small interatomic separation distances [67, 68].

Table 2.1: Parameters of the Finnis-Sinclair potential for bcc iron, determined by Finnis and Sinclair [64, 69].

<table>
<thead>
<tr>
<th>( d ) (Å)</th>
<th>( A ) (eV)</th>
<th>( \beta )</th>
<th>( c ) (Å)</th>
<th>( c_0 )</th>
<th>( c_1 )</th>
<th>( c_2 )</th>
</tr>
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<tr>
<td>3.569745</td>
<td>1.828905</td>
<td>1.8</td>
<td>3.40</td>
<td>1.2371147</td>
<td>-0.3592185</td>
<td>-0.0385607</td>
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</tbody>
</table>

**Dudarev-Derlet “magnetic” EAM potential**

In magnetic transition metals such as bcc iron, the correlations between the atomic magnetic moments significantly contribute to the stability of the crystal structure [33, 31]. Thus, for an accurate representation of the interatomic interactions, the coupling between these moments has to be taken into account. Although various semi-empirical potentials have been derived for bcc iron within the EAM formalism [70, 71, 72, 64], these potentials completely neglect the contribution of magnetism to the stabilization of the bcc structure. Using a combination of the Stoner and the Ginzburg-Landau models, Dudarev and Derlet [73, 74] recently formulated a “magnetic” EAM potential for bcc iron, in which the embedding functional \( F[\rho] \) takes the
form

\[ F[\rho] = -A \sqrt{\rho} - \frac{B}{\ln 2} \left( 1 - \sqrt{\frac{\rho}{\rho_c}} \right) \ln \left( 2 - \frac{\rho}{\rho_c} \right) \Theta(\rho_c - \rho), \]  

(2.49)

where \(A\) and \(B\) are constants, \(\Theta(x)\) is the Heaviside step function, and \(\rho_c\) is the critical electron density at which the effect of magnetism vanishes. The first term in Eq. (2.49), which resembles the density functional of the Finnis-Sinclair formalism, represents the non-magnetic contribution to the electron density, whereas the second term specifically captures the contribution of the local magnetic structure \([73]\).

Pairwise functions \(f(r)\) and \(v(r)\) are represented as summations of cubic knot functions:

\[ f(r) = \sum_{n=1}^{N_f} f_n (r_{nf} - r)^3 \Theta(r_{nf} - r), \]  

(2.50)

and

\[ V(r) = \sum_{n=1}^{N_v} V_n (r_{nv} V - r)^3 \Theta(r_{nv} V - r). \]  

(2.51)

This functional form has the advantage of being continuous up to the second derivative, which guarantees that the energy and the interatomic force smoothly approach zero at the cut-off distance associated with each function.

The Dudarev-Derlet potential has been parameterized using a wide range of material properties, including bulk cohesive energy, lattice constants, elastic constants, and vacancy formation energies corresponding to both bcc and fcc, as well as magnetic and non-magnetic phases \([73]\). The optimal parameter set is listed in Table 2.2.

The major shortcoming of the Dudarev-Derlet potential is that it does not explicitly treat the orientational changes of the atomic magnetic moments. All moments are considered to be collinear, with only the magnitudes of the moments varying according to the local atomic environment. Therefore, the treatment of non-collinear spin configurations at finite temperatures is outside its domain of applicability. To achieve the full benefits of the Dudarev-Derlet
potential, one needs to incorporate the dynamics of the spin orientations explicitly via the MD-SD formalism.

Unless specifically stated otherwise, for the simulations presented in the remainder of the thesis, we use Duadarev-Derlet potential.

Table 2.2: Parameters of the Dudarev-Derlet magnetic EAM potential, determined by Dudarev and Derlet [73].

<table>
<thead>
<tr>
<th>$A$</th>
<th>4.100 199 340 884 8140</th>
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<tr>
<td>$B$</td>
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<td>$f_n$</td>
</tr>
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<td>3.0</td>
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<td>-5.307 049 068 415 3040</td>
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<tr>
<td>$r_{nj}^V$</td>
<td>$V_n$</td>
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</tr>
<tr>
<td>2.3</td>
<td>80.220 695 922 469 8700</td>
</tr>
</tbody>
</table>

2.4.2 Exchange interaction

In lattice-based spin models, the exchange parameters $\{J_{ij}\}$ are generally given by a set of discrete values that correspond to the neighbor distances associated with the underlying lattice structure [21, 20]. For off-lattice systems with unlocalized spins, $J_{ij}$ should be depicted
as a continuous function of the atomic coordinates. In such instances, the common practice is to assume that $J_{ij}$ is a pairwise function of the interatomic distance; i.e. $J_{ij} = J(r_{ij})$ [37]. Recently, Yin et al. [30] discussed the inadequacy of modeling the exchange interaction for itinerant systems as a pairwise function since such model would fail to describe the longitudinal fluctuations in magnetic moments. In principle, the pairwise interaction $J_{ij}$ may depend on the local atomic environment surrounding the atom pair $i$ and $j$ in a nontrivial manner. By introducing local environmental parameters such as the neighbor shell number and the atomic volume, Yin et al. [30] developed a many-body exchange function for bcc iron based on the Locally Self Consistent Multiple Scattering (LSMS) method [75]. However, the proposed exchange function is not suitable for dynamical simulations due to the complications associated with the discontinuity of its derivative at the cut-off distance.

In this thesis, we assume a simple pairwise function for the exchange interaction, which was parameterized by Ma et al. [38] by fitting a continuous function to the first principles data obtained from linear muffin-tin orbitals (LMTO) method [76, 77]. The fitted function takes the form of a third-order polynomial

$$J(r_{ij}) = J_0(1 - r_{ij}/r_c)^3\Theta(r_c - r_{ij}),$$

(2.52)

where the cut-off distance $r_{ij} = 3.75$ Å was chosen to lie between the second and the third nearest neighbor distances of the bcc iron lattice. The optimal value of $J_0$ was found to be 0.90490177 eV. Fig. 2.2 shows the fitted curve and the first principles data set taken from Ref. [76] and [77].

It should be noted that the pairwise function $J(r_{ij})$ has been parameterized in such a way that the magnitudes of the spins $S_i$ and $S_j$ are absorbed into its definition. Therefore, to obtain the correct form of the exchange interaction as defined in the Hamiltonian (2.35),
we divide $J(r_{ij})$ by the respective spin lengths as

$$J_{ij} = J(r_{ij})/S_i S_j.$$  \hfill (2.53)

### 2.4.3 Determining the magnitudes of the spins

To accurately model the time evolution of the spins as described by Eq. (2.37), one needs to choose appropriate values for the magnitudes of the spins. As discussed in section 2.3.3, the effective spin angular momentum associated with each atom is related to its magnetic moment $\mu_i$ via the relationship

$$\mu_i = g \mu_B S_i,$$ \hfill (2.54)

where $\mu_B$ is the Bohr magneton, and $g$ is the electron $g$-factor which is approximately equal to 2.002319. As the magnitude of the atomic moment $\mu_i$ is a quantity that can be obtained through experiments or first-principles calculations, using Eq. (2.54), one can determine the appropriate spin length as $S_i = \mu_i / g \mu_B$. 

Figure 2.2: Pairwise exchange function for bcc iron, parameterized by Ma et al. [38]. Filled circles represent the first principles data set used for parameterization.
Since elemental iron has 4 unpaired $d$ electrons, each atom carries an effective spin value of $4/2$, yielding a magnetic moment approximately equal to $4\mu_B$. However, for the case of the ferromagnetic ground state of bcc iron, the experimentally observed atomic magnetic moment is $2.2\mu_B$ [78]. Such non-integral atomic moments as observed for all $3d$ transition metals is a direct consequence of the itinerant nature of the $3d$ electrons [79, 6, 5]. In transition metals, the energy band of the $3d$ electrons overlaps with the $4s$ energy band. Thus, $3d$ electrons partly possess characteristics of $4s$ electrons, which allows them to become itinerant, hopping or tunneling from one atomic site to another. Consequently, the number of electrons per atom contributing to the atomic magnetic moment is not an integral number, which leads to the experimentally observed values.

As the density of states for the $3d$ electrons strictly depends on the local atomic environment, the effective atomic magnetic moment also varies as the local crystal structure changes. In fact, it has been experimentally verified that the atomic moment of bcc iron increases/decreases as the local atomic volume is increased/decreased [80, 81]. If one can establish a functional relationship between the atomic magnetic moment and some parameter characterizing the local atomic environment, one can dynamically adjust the spin lengths in MD-SD simulations as the local environment changes. Derlet et al. [74] showed that within the framework of the Dudarev-Derlet potential, such a relationship can be established as

$$\mu_i = C \left( 1 - \sqrt{\frac{\rho_i}{\rho_c}} \right)^\gamma,$$

(2.55)

where $C$ and $\gamma$ are constants, and $\rho_i$ is the Dudarev-Derlet density as determined from the Eqs. (2.45) and (2.50), with $\rho_c$ being the cut-off density chosen to be unity. By fitting the above functional form to the results of first-principles calculations, the optimal numerical values for $C$ and $\gamma$ were obtained as 2.929$\mu_B$ and 0.259, respectively.
Since Eq. (2.55) is fitted for the densities of the Dudarev-Derlet potential, it cannot be used in simulations involving other EAM potentials. For our simulations using the Finnis-Sinclair potential, we used a regression relationship between the moment and the volume of the Voronoi polyhedron of the atom [82] established via the Locally Self Consistent Multiple Scattering (LSMS) method [75], which takes the form

\[ \mu_i = 0.063176 V_i - 2.689, \]  

(2.56)

where \( V_i \) is the Voronoi volume of the \( i \)th atom measured in Bohr radius cubed \( (a_0^3) \). Since the use of Eq. (2.56) requires the calculation of the Voronoi volumes for all the atoms during each integration time step, it significantly slows down the time integration.
Chapter 3

Simulation methods

3.1 Metropolis and Wang–Landau importance sampling

Monte Carlo approaches

As discussed in section 2.1.2, the expectation values of thermodynamic quantities in the canonical ensemble can, in principle, be calculated with the formula

$$\langle A \rangle_{NVT} = \frac{\sum_x A(x) e^{-\beta H(x)}}{\sum_x e^{-\beta H(x)}}. \quad (3.1)$$

Unfortunately, summing over the terms in the numerator and the denominator corresponding to all states \(\{x\}\) of the system is impracticable except for extremely small systems. The simplest solution to this problem would be to reduce the number of terms in the summations to a manageable size by randomly selecting a subset of states \(\{x_1, x_2, \ldots, x_M\}\), and estimate \(\langle A \rangle_{NVT}\) as

$$\langle A \rangle_{NVT} \approx \frac{A(x)}{NVT} = \frac{\sum_{i=1}^M A(x_i) e^{-\beta H(x_i)}}{\sum_{i=1}^M e^{-\beta H(x_i)}}. \quad (3.2)$$
However, such a simple sampling strategy would result in a poor estimate of $\langle A \rangle_{NV,T}$ since one might be completely ignoring the states that contribute significantly to the summations. Instead of selecting states completely at random, if one could bias the sampling scheme such that the states that have higher contributions to the summations are chosen more frequently than the others, reasonable estimates can be obtained with only a small number of samples. This strategy of selecting “important” states from a large number of possible states is called “importance sampling”, and the class of simulation methods that utilize this technique is generally known as “importance sampling Monte Carlo” [11, 13, 14].

### 3.1.1 Metropolis sampling method

The Metropolis method [83] is an importance sampling Monte Carlo (MC) technique which uses a Markov process to construct a sequence of states that follows the Boltzmann probability distribution. Given that the system is currently in state $x_m$, the method generates the next state in the sequence $x_n$ according to the transition rate $W(x_m \rightarrow x_n)$, which depends on the energy difference between the two states.

The probability of the system being in state $x_m$ at the Monte Carlo time $t$ obeys the master equation

$$\frac{\partial P_{x_m}(t)}{\partial t} = -\sum_{m \neq n} [P_{x_m}(t)W(x_m \rightarrow x_n) - P_{x_n}(t)W(x_n \rightarrow x_m)]. \quad (3.3)$$

If the system is in equilibrium, $\partial P_{x_m}(t)/\partial t = 0$. A sufficient condition that satisfies this constraint is the principle of detailed balance [11]

$$P_{x_m}(t)W(x_m \rightarrow x_n) = P_{x_n}(t)W(x_n \rightarrow x_m). \quad (3.4)$$
With transition rates in Eq. (3.4) chosen appropriately, one can arrange for the probability distribution of states generated by the Markov process to eventually approach any distribution of interest. As our goal is to achieve Boltzmann distribution, we set the ratio \( P_{x_m}/P_{x_n} \) equal to the ratio between the respective Boltzmann weights and obtain

\[
\frac{W(x_m \rightarrow x_n)}{W(x_n \rightarrow x_m)} = \frac{p_{x_n}}{p_{x_m}} = e^{-\beta(\Delta E)},
\]

(3.5)

where \( \Delta E = H(x_n) - H(x_m) \), the energy difference between the final and the initial states. Eq. (3.5) does not uniquely specify \( W(x_m \rightarrow x_n) \), thus many choices can be made that satisfy this condition. A simple and convenient choice is the famous Metropolis criterion [83]

\[
W(x_m \rightarrow x_n) = \min\left(1, e^{-\beta(\Delta E)}\right).
\]

(3.6)

In the practical implementation of the Metropolis method, one starts with an arbitrary initial state of the system, and sequentially performs a set of “trial moves” on the phase variables which are either accepted or rejected along the way based on the criterion given in Eq.(3.6). Once a trial move is performed, energy difference \( \Delta E \) associated with the proposed transition is calculated. If \( \Delta E < 0 \), the proposed move is immediately accepted. If \( \Delta E > 0 \), a uniformly distributed random number \( r \) with \( r \in [0,1] \) is generated, and the trial state is accepted if \( r < e^{-\beta(\Delta E)} \). Otherwise, the trial state is rejected. The execution of a trial move followed by its subsequent acceptance or rejection constitutes a single Monte Carlo step. Typically, a Metropolis simulation will continue until a desired number of MC steps have been completed. In practice, a certain number of MC steps at the beginning of the sequence is discarded to allow for the system to approach equilibrium. Once in equilibrium, the probability distribution of states being generated by the Markov process will satisfy the Boltzmann distribution. Thus, the Boltzmann factors in Eq. (3.2) will vanish, leading to a
simple expression for estimating ensemble averages:

\[ \langle A \rangle_{NVT} \approx \frac{A(x)_{NVT}}{M} = \frac{1}{M} \sum_{i=1}^{M} A_{x_i}. \] (3.7)

### 3.1.2 Monte Carlo trial moves for coupled spin-lattice systems

For coupled spin-lattice systems, the configurational space that one seeks to sample via Monte Carlo methods consists of \(2N\) phase variables: \(\{x\} = \{r_1, r_2, \cdots, r_N, S_1, S_2, \cdots, S_N\}\). For effectively sampling this configurational space with respect to both atomic coordinates and spins, we employ the following two trial moves.

1. **Single atom displacement move**
   
   Displace the chosen atom \(i\) to a random position \(r_i'\) within a sphere centered at its original position \(r_i\):
   
   \[ r_i' = r_i + R, \quad \text{where} \quad |R| < R_{\text{max}} \]

2. **Single spin rotation move**

   Assign a new random direction to the spin \(S_i\) of the chosen atom \(i\).

During each MC step, we randomly choose an atom and perform one of the above trial moves at random with equal probability. Completion of \(2N\) such MC steps constitute a single “MC sweep”. For the remainder of this thesis, we will use MC sweeps as the basic unit of measuring MC time.

For the case of the Metropolis method, we have observed that the maximum allowed displacement of the atoms, \(R_{\text{max}}\), significantly influences the performance of the simulations. Therefore, during an initial phase of the simulation, we iteratively adjust \(R_{\text{max}}\) such that an average acceptance rate of \(45 - 55\%\) is obtained for the single atom displacement moves.
3.1.3 Wang–Landau sampling method

An inherent downside of the Metropolis sampling is its tendency to get trapped in local free-energy minima that are frequently encountered in systems with complex free energy landscapes. To circumvent this pitfall, different methodologies have been introduced. One popular approach is to perform multiple Metropolis simulations at different temperatures and allow periodic conformational (replica) exchanges between them. This is widely known as parallel tempering or replica-exchange Monte Carlo [84, 85]. Another approach strives to sample microstates from a flat probability distribution (the so-called multicanonical ensemble [86, 87]), where the states have non-Boltzmann weights that are inversely proportional to the *a priori* unknown density of states. Such generalized-ensemble methods hope to escape free energy barriers and avoid long time scales encountered at low temperatures and near phase transitions. To this end, the Wang–Landau (WL) method [88, 89, 90] has emerged as a simple but powerful technique.

The foundation for the Wang–Landau approach is to recognize that the canonical partition function (2.10) can be rewritten as a summation over all energies in the form

$$Z = \sum_E g(E) e^{-\beta E}, \quad (3.8)$$

where $g(E)$ is the density of states. If $g(E)$ is known, the problem is essentially solved since one can directly estimate the ensemble average of any thermodynamic function of $E$ as

$$\langle A(E) \rangle_{NVT} = \frac{\sum_E A(E) g(E) e^{-\beta E}}{\sum_E g(E) e^{-\beta E}}. \quad (3.9)$$

The goal of Wang–Landau sampling is to perform a random walk in the configurational space while iteratively adjusting the density of states. This ultimately leads the accumulation of a uniform histogram in the energy space. Eventually, the Wang-Landau scheme delivers
an estimate for the density of states so that the thermodynamic behavior of the system for
the entire temperature range of interest can be extracted from a single simulation. The
method has been successfully applied to a wide array of intricate problems in condensed
matter and statistical physics including spin glasses, liquid crystals, polymers, protein folding
etc. [91, 92, 93, 94].

The original Wang–Landau algorithm

At the beginning of the Wang–Landau simulation, the desired total energy range $E \in [E_{\text{min}}, E_{\text{max}}]$ for which $g(E)$ should be obtained is determined. For systems with continuous energy domains, the total energy range is divided into bins with size $\delta E$ appropriately chosen according the desired level of resolution in $g(E)$. Since $g(E)$ is unknown in the beginning of the simulation, an initial guess of $g(E) = 1$ is assigned for all energies as a starting point. Then, starting from an arbitrary initial state of the system, a random walk in the configurational space is performed by sequentially generating trial states. During each MC step, a new trial state $x_n$ is generated by applying an MC trial move on the current state $x_m$. The new state is accepted according to the probability

$$P(x_m \rightarrow x_n) = \min \left[ 1, \frac{g(E(x_m))}{g(E(x_n))} \right]. \quad (3.10)$$

If the trial state $x_n$ is accepted, the density of states entry for $E(x_n)$ is updated as $g(E(x_n)) \rightarrow g(E(x_n)) \times f$, where $f$ is the “modification factor” which we initially set to $f_0 = e^1$. If the trial state is rejected, the entry for the old state is updated as $g(E(x_m)) \rightarrow g(E(x_m)) \times f$.

The random walk is continued until all energy bins have been roughly visited equal number of times. To check whether this condition is satisfied, a histogram $H(E)$ of the visited energies is maintained and updated with each trial move. When all the entries in the histogram are greater than a certain $x\%$ of the average histogram value, the histogram
is considered to be “flat”. At this point, the modification factor is reduced by $f \to \sqrt{f}$, the histogram is reset to zero, and another iteration of the random walk is initiated. This process is repeated until the modification factor $f$ reaches a predefined terminal value, say $f_{\text{final}} = e^{1 \times 10^{-8}}$.

**Replica exchange framework for massively parallel Wang-Landau sampling**

Over the years, various attempts have been made to improve the efficiency of the Wang–Landau method, either with the aid of efficient MC trial moves, or by accelerating the convergence of the iterative method (see Refs. [95, 96, 97] for examples). Nevertheless, in order to exploit the power of the modern high performance computing systems and adapt the method to even larger-scale systems with increased complexity, an efficient parallelization scheme is essential.

The recently introduced generic framework for massively parallel Wang–Landau sampling [46, 47, 48, 49] combines the advantages of the Wang-Landau dynamics with the concept of conformational swapping in parallel tempering [84, 85]. In this approach, the global energy range $[E_{\text{min}}, E_{\text{max}}]$ is divided into $h$ number of smaller subwindows, each of which overlaps with its nearest neighbors on both sides with an overlap ratio $o$ (A schematic diagram is shown in Fig. 3.1). In each subwindow, $m$ number of random walkers are employed. Each walker has its own $g(E)$ and $H(E)$, which are updated independently. Once all walkers within an energy subwindow have individually satisfied the flatness criterion, their estimates for $g(E)$ are averaged out and distributed among each other before simultaneously proceeding to the next iteration. The simulation is terminated when the modification factors for all subwindows have reached the terminal value $f_{\text{terminal}}$.

During the simulation, after every $n$ number of MC steps, replica exchanges between walkers in adjacent energy subwindows are proposed. For every walker $i$, a “swap partner” $j$ is chosen randomly from one of the adjacent subwindows. If $x$ and $y$ are the current
configurations of the walkers $i$ and $j$, the two configurations are interchanged according to the probability

$$P_{RE} = \min \left[ 1, \frac{g_i(E(x))g_j(E(y))}{g_i(E(y))g_j(E(x))} \right],$$

(3.11)

where $g_i(E(x))$ is the current estimate for the density of states of the walker $i$ with energy $E(x)$.

At the end of the simulation, the parallel Wang–Landau method provides multiple, overlapping fragments of $g(E)$. These fragments are joined at points where the slopes of $\ln g(E)$ (i.e. $d \ln g(E)/dE$, the inverse microcanonical temperature) best coincide. This practice reduces the introduction of artificial kinks in the combined $g(E)$ due to the joining process and eliminates resultant errors in thermodynamic quantities [47].

Figure 3.1: Partitioning the global energy range into seven subwindows with overlap $o = 75\%$. The arrows indicate the communication pathways between neighboring subwindows for the replica-exchange attempts.
3.2 Time integration algorithm for combined molecular and spin dynamics

The equations of motion (2.36) can be written in the form of an operator equation

\[ \frac{dy(t)}{dt} = \hat{L} y(t), \quad (3.12) \]

where \( y(t) = \{ r_i(t), v_i(t), S_i(t) \} \) denotes the complete set of phase variables consisting of the positions, velocities and the spins, and \( \hat{L} \) is the the generalized Liouville operator \([98]\) which takes the form

\[ \hat{L} = \sum_{i=1}^{N} \left[ v_i \cdot \frac{\partial}{\partial r_i} + \frac{f_i}{m} \cdot \frac{\partial}{\partial v_i} + \left( \frac{1}{\hbar} S_i \times H_{i}^{\text{eff}} \right) \cdot \frac{\partial}{\partial S_i} \right]. \quad (3.13) \]

The formal solution to Eq. (3.12) is

\[ y(t + \tau) = e^{\hat{L}\tau} y(t), \quad (3.14) \]

where \( \tau \) is the integration time step, and \( e^{\hat{L}\tau} \) is the exponential operator which fully determines the time evolution of the microscopic phase variables. Unfortunately this operator cannot be evaluated exactly, thus one has to rely on approximate solutions which involve the decomposition of the operator into a series of sub-operators, where the respective operations are trivial enough to be evaluated analytically. As the first step, we write the Liouville operator \( \hat{L} \) as a sum of three terms,

\[ \hat{L} = \hat{L}_r + \hat{L}_v + \hat{L}_s, \quad (3.15) \]

where \( \hat{L}_r = \sum_i v_i \cdot \partial/\partial r_i \) which only acts on positions, \( \hat{L}_v = \sum_i (f_i/m) \cdot \partial/\partial v_i \) which only acts on velocities, and \( \hat{L}_s = \sum_i (1/\hbar) (S_i \times H_{i}^{\text{eff}}) \cdot \partial/\partial S_i \) which only operates on spins. The
solution given by Eq. (3.14) now takes the form,

\[ y(t + \tau) = e^{(\hat{L}_r + \hat{L}_v + \hat{L}_s) \tau} y(t). \]  

(3.16)

Since \( L_r, L_v, \) and \( L_s \) are noncommuting operators, the composite exponential operator \( e^{(\hat{L}_r + \hat{L}_v + \hat{L}_s) \tau} \) cannot be simply replaced by the product of individual exponential operators, \( e^{L_r \tau} e^{L_v \tau} e^{L_s \tau} \). However, one can obtain an approximate factorization of \( e^{(\hat{L}_r + \hat{L}_v + \hat{L}_s) \tau} \) based on the method of Suzuki-Trotter (ST) decomposition for noncommuting operators [23]. For a pair of arbitrary noncommuting operators \( A \) and \( B \), ST decomposition yields [25]

\[ e^{(A + B) \tau} = e^{A \tau} e^{B \tau} + \mathcal{O}(\tau^2) \]  

(3.17)

to first order, and

\[ e^{(A + B) \tau} = e^{A \tau/2} e^{B \tau} e^{A \tau/2} + \mathcal{O}(\tau^3) \]  

(3.18)

to second order. Grouping \( \hat{L}_r \) and \( \hat{L}_s \) together as a single operator, one can use the second order formula to decompose \( e^{(\hat{L}_v + \hat{L}_r + \hat{L}_s) \tau} \) as

\[ e^{(\hat{L}_v + (\hat{L}_r + \hat{L}_s)) \tau} = e^{\hat{L}_v \tau/2} e^{(\hat{L}_r + \hat{L}_s) \tau} e^{\hat{L}_v \tau/2} + \mathcal{O}(\tau^3), \]  

(3.19)

Eq. (3.19) can be further decomposed by factorizing \( e^{(\hat{L}_r + \hat{L}_s) \tau} \) in a similar manner to yield

\[ e^{(\hat{L}_r + \hat{L}_v + \hat{L}_s) \tau} = e^{\hat{L}_r \tau/2} e^{\hat{L}_v \tau/2} e^{\hat{L}_s \tau} e^{\hat{L}_r \tau/2} e^{\hat{L}_v \tau/2} + \mathcal{O}(\tau^3). \]  

(3.20)

Note that one can decompose the operator \( e^{(\hat{L}_r + \hat{L}_v + \hat{L}_s) \tau} \) in alternative ways and arrive at different operator sequences (in total, 6). However, the sequence given in Eq. (3.20) leads to the minimal number of force and effective field calculations, and hence is the most computationally efficient. We also note that while it is possible to obtain higher order decompositions [24]
of $e^{(\hat{L}_r+\hat{L}_v+\hat{L}_s)\tau}$, the accuracy obtained through the second-order decomposition is sufficient for the simulations described in this thesis (See section 3.9 for details).

The operations $e^{\hat{L}_r\tau y(t)}$ and $e^{\hat{L}_v\tau y(t)}$ have simple explicit solutions. In order to derive the solution for $e^{\hat{L}_r\tau y(t)}$, we first write $\hat{L}_r$ in terms of its individual components: $\hat{L}_r = \sum_i \hat{L}_{ri}$, where $\hat{L}_{ri} = v_i \cdot \partial / \partial r_i$, and factorize $e^{\hat{L}_r\tau}$ as

$$e^{\hat{L}_r\tau y(t)} = e^{(\tau \sum_i \hat{L}_{ri}) y(t)} = \prod_i e^{(\tau \hat{L}_{ri}) y(t)}$$

Note that the above decomposition is only possible since the individual operators $\{\hat{L}_{ri}\}$ commute with each other. $e^{(\tau \hat{L}_{ri})}$ only operates on $r_i$, and can be evaluated as

$$e^{(\tau \hat{L}_{ri})} r_i = e^{(\tau v_i \cdot \partial / \partial r_i)} r_i = \sum_{n=0}^{\infty} \frac{1}{n!} (\tau v_i \cdot \partial / \partial r_i)^n r_i = r_i + v_i \tau$$

Eq. (3.21) combined with (3.22) yields

$$e^{\hat{L}_r\tau y} = \{r_i + v_i \tau, v_i, S_i\}$$

Similarly, we can show that

$$e^{\hat{L}_v\tau y} = \left\{ r_i, v_i + \frac{f_i}{m} \tau, S_i \right\}.$$
find an approximate solution for $e^{\hat{L}_s \tau}$. Krech et al. [24] and Tsai et al. [25] discuss the decomposition of $e^{\hat{L}_s \tau}$ for lattice-based spin systems by separating the lattice into a set of non-interacting sublattices. However, such decompositions cannot be directly applied to off-lattice systems where the neighbors of the spins are subject to change with time. Therefore, following the method proposed by Omelyan et al. [37], we write the operator $e^{\hat{L}_s \tau}$ in terms of its components as $e^{\hat{L}_s \tau} = \exp \left( \tau \sum_i \hat{L}_s \right)$, and iteratively apply the second order ST formula to obtain

$$e^{\hat{L}_s \tau} = e^{\hat{L}_{s1} \tau/2} \cdots e^{\hat{L}_{sN-1} \tau/2} e^{\hat{L}_{sN} \tau} e^{\hat{L}_{sN-1} \tau/2} \cdots e^{\hat{L}_{s1} \tau/2} + O(\tau^3). \quad (3.25)$$

The operator $e^{\hat{L}_{si} \tau}$ only acts on the $i$th spin, and has a simple analytical solution [24] given by

$$e^{\hat{L}_{si} \tau} = \hat{h}_i \left( \hat{h}_i \cdot S_i \right) + \left[ S_i - \hat{h}_i \left( \hat{h}_i \cdot S_i \right) \right] \cos \left( \frac{\tau}{\hbar} |\vec{H}_{\text{eff}}^i| \right) + \left( S_i \times \hat{h}_i \right) \sin \left( \frac{\tau}{\hbar} |\vec{H}_{\text{eff}}^i| \right), \quad (3.26)$$

where $\hat{h}_i = \vec{H}_{\text{eff}}^i / |\vec{H}_{\text{eff}}^i|$. In essence, Eq. (3.26) denotes a rotation of the $i$th spin around $\vec{H}_{\text{eff}}^i$ by an angle $(\tau / \hbar) |\vec{H}_{\text{eff}}^i|$. Thus, in practice, the operation $e^{\hat{L}_s \tau} y$ is performed as a series of spin rotations, strictly following the order specified by Eq. (3.25). Since these rotations do not change the norm of the spin vectors, spin lengths are exactly conserved during the integration process. Moreover, according to Eq. (3.26), $\vec{H}_{\text{eff}}^i \cdot \left( e^{\hat{L}_{si} \tau} S_i \right) = \vec{H}_{\text{eff}}^i \cdot S_i$, which confirms the exact conservation of energy during the rotations.

The sequence of operations given by Eq. (3.20), along with the respective propagators defined in Eq. (3.23), (3.24) and (3.25), describes a single iteration of our time integration algorithm. In the absence of spin degrees of freedom, the sequence reduces to $e^{\hat{L}_v \tau/2} e^{\hat{L}_s \tau} e^{\hat{L}_v \tau/2}$, which is equivalent to the velocity-Verlet algorithm [25]. As the operators $e^{\hat{L}_v \tau/2}$ and $e^{\hat{L}_s \tau}$ change the atomic positions and spins respectively, prior to performing the last operation of the sequence $e^{\hat{L}_v}$, one needs to recalculate all interatomic forces. This represents the
most computationally expensive step of the integration algorithm, and special techniques are required in order to speed up the execution (See section 3.4).

### 3.3 Periodic boundary conditions

To overcome the surface effects that occur due to the finite size of the system, we employ periodic boundary conditions. The bulk system is modeled as an infinite lattice made out of identical copies of the simulation box (See Fig. 3.2). During the course of the simulation, motion of the atoms and spins contained in the “primary” simulation box is exactly replicated in all the periodic copies of the system. As a result, when an atom moves out of the primary simulation box from one side, one of its “images” from an adjacent box will enter the primary box through the opposite side. In the practical implementation of this approach, only the positions, velocities and spins of the atoms in the primary simulation box are stored in memory. Therefore, whenever an atom leaves the simulation box from one side, the same atom will reenter from the opposite side. In order for this approach to work, the linear size of the simulation box $L$ should be at least twice the cut-off radius of the interaction potential. When this condition is satisfied, the interaction between any two atoms is computed as the interaction between their closest periodic images.

### 3.4 Linked list algorithm

The most computationally demanding operations in MD-SD and MC simulations are the calculations of various interactions associated with the atoms (e.g. interatomic forces, effective fields and energies). In order to compute pairwise interactions for a particular atom $i$, one needs to consider the contributions from all other atoms that are separated from $i$ by distances less than the cut-off distance $r_c$ of the interaction potential. (We recollect that all
interaction terms in our Hamiltonian are constructed from short-range pairwise functions.)

In the brute force implementation of this calculation, one would sequentially loop over all
the atoms in the simulation box and determine each atom’s involvement in the calculation
“on-the-fly” based on its separation distance from atom $i$. The total time taken to repeat
this process for all the $N$ atoms in the system would scale as $O(N^2)$.

Various techniques have been introduced to reduce the computational demands associated
with the calculation of pairwise interactions. Among them, the linked list method [99]
stands out as one of the most efficient and widely used techniques in large-scale MD and
MC simulations. The linked list method partitions the cubic simulation box into cells of
side length $l$ greater than or equal to the cut-off distance $r_c$. The rationale behind this
decomposition is that all the atoms that interact with a particular atom $i$ can be found in
the cell which the atom belongs to, and its adjacent cells. (See Fig. 3.3) Whenever the atomic
coordinates $\{r_i\}$ are changed during the simulation, all the atoms in the simulation box are
assigned to appropriate cells, based on their positions within the box. During this process,
Figure 3.3: Linked list method in two dimensions. The simulation box is divided into a $4 \times 4$ cell structure. To find all the atoms that are within the cut-off radius $r_c$ of the atom $i$, it is sufficient to search the cell that the atom belongs to (dark-shaded), and its adjacent cells (light-shaded).

A linked list of atom indices is created to keep track of atoms in each cell. This linked list consists of two arrays; HEAD and LIST. The array HEAD has one element corresponding to each cell in the simulation box. HEAD[$i$] contains the index of the first atom sorted into $i$th cell. HEAD[$i$] also represents an index in the LIST array, where it contains the index of the next atom sorted into $i$th cell. Then again the LIST array element LIST[HEAD[$i$]] contains the index of the next atom in the cell, and so on. The list is usually terminated by adding a dummy index (say, 0) as the last value of the chain. Thus, by starting from an element in the HEAD array, the algorithm can follow through the linked list indices to find all the atoms in the corresponding cell. When the algorithm encounters the dummy index, it simply terminates the search. Fig. 3.4 illustrates this sorting procedure for atoms in two neighboring cells. To find all the atoms that interact with a particular atom, the algorithm first scans through the linked list chain of its own cell, and then moves on to the linked list chains of the
nearest neighbor cells. This procedure eliminates significant amount of unnecessary pairwise distance calculations that would result from its brute-force counterpart.

3.5 Parallel algorithm for spin dynamics

An effective parallelization scheme is an essential ingredient for achieving the best possible performance and scalability in large-scale atomistic simulations. Parallelization of MD simulations have been extensively explored with regard to three decomposition schemes, namely, atomic, force, and domain decompositions [100]. Although these strategies can be readily adapted to MD-SD simulations for parallelizing the MD component, the full potential of parallel processing cannot be achieved unless the spin dynamics component is also parallelized.

The major bottleneck in parallelizing spin dynamics is the sequential order in which spin rotations are performed in Eq. (3.25). The key to develop a parallelization scheme for spin evolutions is to rearrange this sequence in such a way that we can group certain
individual spin evolution operators together and perform rotations in parallel. Such grouping of operators is indeed possible since the interaction range of each spin is limited by the cut-off distance of the pairwise exchange interaction $J(r_{ij})$. Based on this idea, Ma et al. [101] recently introduced a generic approach for parallelizing spin dynamics, which is equally applicable for both lattice-based and spatially disordered spin systems. In this approach, spin groups are formed by exploiting the idea of the spatial decomposition of the simulation box described in section 3.4. As the side length of each cell is greater than the cut-off distance of the exchange interaction, a particular spin can only interact with the spins in its own cell and the spins in the adjacent cells. These cells can then be arranged into groups in such a way that the spins in a particular cell do not interact with the spins in other cells that belong to the same group. Fig. 3.5 shows the assignment of groups for a two dimensional system with 25 cells. The arrangement consists of 8 groups labeled A to H.

![Figure 3.5: Grouping spins for parallel processing in a two dimensional simulation box with 25 cells. Periodic images of the cells on the boundary of the simulation box are also shown.](image)

To facilitate the discussion further, let us denote by $\hat{L}_X$ the Liouville operator associated with the dynamics of all the spins in an arbitrary group $X$. The functional form of $\hat{L}_X$ is
given by
\[ \hat{L}_X = \sum_{i \in X} \left( \frac{1}{\hbar} \right) (\mathbf{S}_i \times \mathbf{H}_{i}^{\text{eff}}) \cdot \partial / \partial \mathbf{S}_i. \] (3.27)

Then, the exponential operator \( e^{\hat{L}_X \tau} \) determines the time evolution of the spins in the group \( X \) as a whole. Similarly, the Liouville operator \( \hat{L}_\ell \) associated with the spins in an arbitrary cell \( \ell \) takes the form
\[ \hat{L}_\ell = \sum_{j \in \ell} \left( \frac{1}{\hbar} \right) (\mathbf{S}_j \times \mathbf{H}_{j}^{\text{eff}}) \cdot \partial / \partial \mathbf{S}_j, \] (3.28)

and the corresponding time evolution operator is given by \( e^{\hat{L}_\ell \tau} \). With the aid of the operators defined above, we now demonstrate the parallelization strategy for the two dimensional system depicted in Fig. 3.5. Using the second order ST decomposition iteratively, we can factorize the total spin evolution operator \( e^{\hat{L}_s \tau} \) in terms of the group operators:
\[ e^{\hat{L}_s \tau} = e^{\hat{L}_A(\tau/2)} e^{\hat{L}_B(\tau/2)} \ldots e^{\hat{L}_G(\tau/2)} e^{\hat{L}_{H\ell}(\tau/2)} \ldots e^{\hat{L}_B(\tau/2)} e^{\hat{L}_A(\tau/2)} + O(\tau^3). \] (3.29)

As the cells that belong to the same group are independent of each other, the exponential operator associated with each group can be factorized as a product of exponential operators corresponding to the constituent cells. For instance, in the case of group \( A \) which consists of cells \( \{1, 3, 11, 13\} \), one obtains
\[ e^{\hat{L}_A \tau} = e^{(\hat{L}_1 + \hat{L}_3 + \hat{L}_{11} + \hat{L}_{13}) \tau} = e^{\hat{L}_1 \tau} e^{\hat{L}_3 \tau} e^{\hat{L}_{11} \tau} e^{\hat{L}_{13} \tau}. \] (3.30)

(Note that the exact order of operators in Eq. (3.30) is irrelevant.) These cell operations can be performed independently of each other, which allows us to treat them in parallel using concurrent threads. However, as the spins within the same cell do interact with each other, the time evolution of spins in the same cell has to be processed sequentially following an ST sequence similar to Eq. (3.25). 

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In our MD-SD code, we have implemented the above parallel spin dynamics scheme under a shared memory architecture using OpenMP [102]. For parallelizing the MD component, we have adopted a simple force decomposition scheme [100], in which the workload associated with the calculation of interatomic forces is distributed among concurrent threads.

### 3.6 Generating initial configurations for microcanonical MD-SD simulations

A typical problem of interest with regard to atomistic dynamic simulations is the calculation of deterministic time-dependent properties (e.g. dynamic structure factor, transport coefficients etc.) for a system in equilibrium at a given temperature $T$. A convenient strategy is to compute these quantities from the time series obtained from a microcanonical dynamic simulation, which is, in turn, initiated from an equilibrium state drawn from the canonical ensemble at temperature $T$. Finally, averaging over the results of multiple simulations started from different initial states yields good estimates of the respective canonical ensemble averages.

For calculating the dynamic properties of our coupled spin-lattice system (see chapter 4 for example), we adopt the same technique described above. As for generating the initial states for these simulations, we adhere to the following step-by-step procedure. First, we equilibrate the subspace consisting of positions and spins using the Metropolis MC method. For the system sizes and the temperature range considered in this thesis, we find that an MC run of $2000 - 3000$ sweeps is sufficient for this purpose. As the second step, we assign initial velocities to the atoms based on the Maxwell-Boltzmann distribution at the desired temperature $T$. Finally, we carry out a short microcanonical MD-SD equilibration run (typically $\sim 1000$ time steps with $\tau = 1$ fs), which would ultimately bring the whole system
to the equilibrium by resolving any inconsistencies between the position-spin subspace and the velocity distribution. A pictorial representation of this procedure is shown in Fig. 3.6.

Figure 3.6: The general recipe followed in microcanonical MD-SD simulations.

### 3.7 Controlling temperature in canonical simulations

To perform dynamic simulations in the canonical ensemble, one needs to utilize a mechanism for explicitly controlling the temperature of the system. In the context of MD simulations, various deterministic and stochastic approaches have been proposed [54, 52, 53] for controlling the lattice temperature. In deterministic approaches (e.g. Nosé-Hoover [103]), the dynamic system is extended to include an additional fictitious degree of freedom which represents the thermal reservoir. The reservoir carries its own “thermal inertia” and dynamically exchange energy with the system in order to maintain the system in equilibrium at the desired temperature. In stochastic approaches (e.g. Andersen thermostat [104], Langevin dynamics [60]), the atoms undergo fictitious collisions with an imaginary heat bath particles that drive the system towards the equilibrium. In the Andersen’s approach, atoms are randomly chosen and new velocities are assigned based on the Maxwell-Boltzmann distribution.
In Langvein dynamics, during every time step, each atom in the system is subjected to a frictional force and a random thermal force that are related by the fluctuation-dissipation theorem [60]. Langevin dynamics was originally proposed as an approach for modeling the viscous forces due to implicit solvent molecules [60], but is now being commonly used in a broader context for modeling the stochastic motion of atoms in the “sea” of imaginary heat bath particles. Adaptations of Langevin dynamics have been also applied to classical spin systems [105, 106] for controlling the spin temperature.

In this thesis, we adopt Langevin dynamics approach for controlling both lattice and spin temperatures. For Langevin spin dynamics, we adhere to the formulation developed by Ma et al. [106].

### 3.7.1 Langevin dynamics for translational degrees of freedom

Langevin equation of motion for translational degrees of freedom [60] is given by

\[
m \frac{d\mathbf{v}_i}{dt} = -\eta m \mathbf{v}_i + \mathbf{f}_i + \mathbf{R}_i(t),
\]

where \( \mathbf{f}_i = -\nabla_{\mathbf{r}_i} \mathcal{H} \) is the familiar interatomic force, and \( \eta \) is the coefficient of dissipative friction which characterizes the “viscosity” of the system. \( \mathbf{R}_i(t) \) is the Gaussian distributed random thermal force which satisfies the condition

\[
< R_{i\alpha}(t) R_{j\beta}(t') > = \lambda_l \delta_{ij} \delta_{\alpha\beta} \delta(t - t'),
\]

with \( T \) being the temperature and \( \alpha, \beta = x, y, z \). The friction coefficient \( \eta \) is related to the random force via the fluctuation-dissipation theorem: \( \lambda_l = 2\eta k_B m T \).

Langevin dynamics approach can be directly incorporated into the MD-SD formalism by replacing the deterministic velocity differential equation (2.36b) with Eq. (3.31). Due to the
discretization of time in the integration algorithm, the delta function \( \delta(t - t') \) in Eq. (3.32) has to be replaced with \( 1/\tau \). In the practical implementation of this method, during each time step, we evaluate the Cartesian components of the stochastic force \( \mathbf{R}_i \) using the expression \( R_{i\alpha} = r_n \sqrt{\lambda_l/\tau} \), where \( r_n \) is a random variable sampled from the standard normal distribution.

### 3.7.2 Langevin spin dynamics

In the Langevin spin dynamics approach [106], one replaces the deterministic spin dynamics equation (2.37) by

\[
\frac{d\mathbf{S}_i}{dt} = \frac{1}{\hbar} \left[ \mathbf{S}_i \times (\mathbf{H}^\text{eff}_i + \mathbf{h}_i) - \gamma \mathbf{S}_i \times (\mathbf{S}_i \times \mathbf{H}^\text{eff}_i) \right],
\]

(3.33)

where \( \mathbf{H}^\text{eff}_i = -\nabla_{\mathbf{S}_i} \mathbf{H} \) is the effective field, \( \gamma \) is a damping constant, and \( \mathbf{h}_i \) is the delta-correlated random field that satisfies

\[
< h_{i\alpha}(t) h_{j\beta}(t') > = \lambda_s \delta_{ij} \delta_{\alpha\beta} \delta(t - t'),
\]

(3.34)

with \( \lambda_s \) given by the fluctuation-dissipation relation, \( \lambda_s = 2\gamma \hbar k_B T \).

In section 3.2, we presented a simple analytical solution for the rotation operation \( e^{L_{\tau} S_i} \) associated with the deterministic spin dynamics equation (2.37). Unfortunately, in the case of the Langevin spin dynamics equation, such an explicit solution does not exist. Therefore, it is no longer beneficial to decompose the composite spin evolution operator \( e^{L_{s,\tau}} \) into its individual atomic components \( \{e^{L_{s,i\tau}}\} \), as in Eq. (3.25). However, it is possible to find an alternative ST decomposition of \( e^{L_{s,\tau}} \) such that its components have simple analytical solutions.
As the first step towards devising this new decomposition scheme, we separate the deterministic and stochastic parts of Eq. (3.33) and rewrite it as

\[
\frac{dS_i}{dt} = \hat{L}_{d_i} S_i + \hat{L}_{t_i} S_i, \tag{3.35}
\]

where the operator \( \hat{L}_{d_i} \) governs the deterministic spin rotation and the dissipation, as given by

\[
\hat{L}_{d_i} = \frac{1}{\hbar} \left[ S_i \times H_{\text{eff}}^i - \gamma S_i \times (S_i \times H_{\text{eff}}^i) \right] \cdot \frac{\partial}{\partial S_i}, \tag{3.36}
\]

and the operator \( \hat{L}_{t_i} \) represents the random thermal fluctuations, as given by

\[
\hat{L}_{t_i} = \frac{1}{\hbar} [S_i \times h_i] \cdot \frac{\partial}{\partial S_i}. \tag{3.37}
\]

The motivation behind this separation is that it is possible to find explicit analytical forms for the time evolution operators corresponding to both \( \hat{L}_{d_i} \) and \( \hat{L}_{t_i} \). We can easily identify that the analytical expression for \( e^{\hat{L}_{t_i} \tau} S_i \) should have the same functional form as the solution to the conventional spin dynamics equation (2.37). Thus, the explicit form of \( e^{\hat{L}_{t_i} \tau} S_i \) can be obtained via Eq. (3.26) by simply replacing \( H_{\text{eff}}^i \) with \( h_i \). One can also derive an explicit analytical form for \( e^{\hat{L}_{d_i} \tau} S_i \) by transforming Eq. (3.36) into spherical coordinates and separating it into polar and azimuthal components [106]. The resulting expression is given by

\[
e^{\hat{L}_{d_i} \tau} S_i = \frac{2 |S_i| H_{\text{eff}}^i |e^\xi \cos \zeta + 2 |S_i \times H_{\text{eff}}^i|}{|H_{\text{eff}}^i| \left[ 1 + e^{2\zeta} + \chi (1 - e^{2\zeta}) \right]} \frac{e^\xi \sin \zeta + H_{\text{eff}}^i |S_i| \left[ 1 - e^{2\zeta} + \chi (1 + e^{2\zeta} - 2 e^\xi \cos \zeta) \right]}{|H_{\text{eff}}^i| \left[ 1 + e^{2\zeta} + \chi (1 - e^{2\zeta}) \right]}, \tag{3.38}
\]

where \( \xi = |H_{\text{eff}}^i| \tau / \hbar, \zeta = -|H_{\text{eff}}^i| |S_i| \gamma \tau / \hbar, \) and \( \chi = (S_i \cdot H_{\text{eff}}^i) / (|S_i||H_{\text{eff}}^i|) \).

With solutions to both \( e^{\hat{L}_{d_i} \tau} S_i \) and \( e^{\hat{L}_{t_i} \tau} S_i \) in hand, we now move on to devising a numerical solution for the time evolution of a system of spins governed by the Langevin spin dynamics equation. If we denote the complete set of spin variables as \( y = \{S_1, S_2, \cdots, S_N\} \),
the equations of motion for all spins can be written in the concise form

\[
\frac{dy}{dt} = \left( \hat{L}_d + \hat{L}_t \right) y,
\]  

where

\[
\hat{L}_d = \sum_i \hat{L}_{d,i}, \quad \text{and} \quad \hat{L}_t = \sum_i \hat{L}_{t,i}.
\]  

The formal solution to Eq. (3.39) takes the form

\[
y(t + \tau) = e^{(\hat{L}_d + \hat{L}_t) \tau} y(t).
\]  

Using the second order ST decomposition, we can factorize the exponential operator \( e^{(\hat{L}_d + \hat{L}_t) \tau} \) as

\[
e^{(\hat{L}_d + \hat{L}_t) \tau} = e^{\hat{L}_d(\tau/2)} e^{\hat{L}_t \tau} e^{\hat{L}_d(\tau/2)} + O(\tau^3).
\]

As the components of \( \hat{L}_t \) commute with each other, \( e^{\hat{L}_t \tau} \) can be factorized as a product of individual exponential operators: \( e^{\hat{L}_t \tau} = \prod_i e^{\hat{L}_{t,i} \tau} \). Thus, the individual operations \( e^{\hat{L}_{t,i} \tau} S_i \) can be performed independently of each other, preferably in parallel using concurrent threads. However, since the components of \( \hat{L}_d \) do not commute, one needs to employ the second order ST formula to decompose \( e^{\hat{L}_d \tau} \) down to the level of its individual atomic components, so that the analytical expression for \( e^{\hat{L}_{d,i} \tau} S_i \) can be exploited. We accomplish this by adopting the parallel decomposition scheme discussed in section 3.5.

As the time integration is performed as a series of spin rotations, this algorithm exactly conserve the magnitudes of the spin vectors.
3.8 Characterizing collective excitations

In MD and SD simulations, time-dependent correlation functions of the microscopic dynamical variables are integral to the study of the collective dynamical behavior of the system [53, 17]. Fourier transforms of these quantities directly yield information regarding the frequency spectra and the lifetimes of the respective collective excitations (e.g. lattice vibrations, spin waves etc.).

Let us define a microscopic dynamical variable $A(r, t)$ as

$$A(r, t) = \sum_{i=1}^{N} a_i(t) \delta [r - r_i(t)], \quad (3.43)$$

where $a_i$ is some physical quantity associated with the atom $i$, such as mass, velocity, spin etc. The spatial Fourier transform of $A(r, t)$ is

$$A(q, t) = \int A(r, t) e^{-iq \cdot r} d\mathbf{r} = \sum_{i=1}^{N} a_i(t) e^{-iq \cdot r_i(t)}. \quad (3.44)$$

For a spatially homogeneous system in thermal equilibrium, the space-displaced, time-displaced autocorrelation function of $A(r, t)$ takes the form

$$C_{AA}(r, t) = \langle A(r', t)A(r'', 0) \rangle, \quad (3.45)$$

where $r = r' - r''$. The spatial Fourier transform of $C_{AA}(r, t)$ is

$$F_{AA}(q, t) = \int C_{AA}(r, t) e^{-iq \cdot r} d\mathbf{r} = \left\langle \sum_{i=1}^{N} \sum_{j=1}^{N} a_i(t)a_j(0) e^{-iq \cdot [r_i(t) - r_j(0)]} \right\rangle, \quad (3.46)$$
which can be expressed in terms of the spatial Fourier components of the dynamical variable $A(r, t)$ as

$$F_{AA}(q, t) = \langle A(q, t)A(-q, 0) \rangle . \quad (3.47)$$

Eq. (3.47) provides a practical means of estimating $F_{AA}(q, t)$ from the trajectories of MD and SD simulations. During the course of the simulation, spatial Fourier components $A(q, t)$ can be computed “on the fly” and accumulated for post processing. Since the system is in equilibrium throughout the simulation, each point in the time series can be considered as a different time origin. Thus, the ensemble average in Eq. (3.47) can be estimated by averaging over different starting points evenly spaced in time, i.e.

$$F_{AA}(q, t) \approx \frac{1}{n+1} \sum_{i=0}^{n} A(q, t+i\Delta t)A(-q, i\Delta t), \quad (3.48)$$

where $\Delta t$ is the time interval between two consecutive samples, and $n = (t_{\text{max}} - t)/\Delta t$ with $t_{\text{max}}$ being the total integration time.

To increase the accuracy of the estimate, one can average over the results for equivalent wave vectors by considering the symmetry of the system. For instance, in systems with cubic symmetry, lattice directions $\{[1 0 0], [0 1 0], [0 0 1]\}$ are equivalent, so are $\{[110], [011], [101]\}$, and $\{[111], [\overline{1}11], [\overline{1}\overline{1}1]\}$. Thus, the results for the wave vectors along these equivalent directions can be averaged.

The accuracy of the estimate can be further enhanced by averaging over multiple independent MD-SD runs starting from different initial configurations drawn from the canonical ensemble (Refer section 3.6).
3.8.1 Lattice vibrations

Let us consider the case $a_i = 1$ in Eq. (3.43). The corresponding dynamical variable is the microscopic atom density

$$
\rho_n(r, t) = \sum_i \delta [r - r_i(t)].
$$

(3.49)

The spatial Fourier transform of the space-displaced, time-displaced density-density correlation function, namely, the intermediate scattering function [44] then takes the form

$$
F_{nn}(q, t) = \frac{1}{N} \langle \rho_n(q, t) \rho_n(-q, 0) \rangle,
$$

(3.50)

where $\rho_n(q, t) = \sum_i e^{-iq \cdot r_i(t)}$. The factor $1/N$ is introduced for normalization purposes.

The power spectrum of the intermediate scattering function

$$
S_{nn}(q, \omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} F_{nn}(q, t)e^{-i\omega t}dt,
$$

(3.51)

is called the “density-density dynamic structure factor” for the momentum transfer $q$ and frequency (energy) transfer $\omega$. $S_{nn}(q, \omega)$ is directly related to the differential cross section measured in inelastic neutron scattering experiments [44], and hence provides a means of comparison between the simulational and experimental results. Local density fluctuations in a system are caused by the thermal diffusion of atoms as well as vibrational modes related to the propagating lattice waves [107]. For liquid systems, the thermal diffusive mode can be identified as a peak in $S_{nn}(q, \omega)$ centered at $\omega = 0$, whereas for solids this peak will disappear due to the absence of thermal diffusion [107]. Peaks in $S_{nn}(q, \omega)$ at non-zero frequencies can be uniquely associated with vibrational modes with the corresponding frequencies and wave vectors.
In crystalline solids, wave propagation along certain lattice directions of high symmetry (e.g. [100], [110] and [111] in cubic crystals) is characterized by planes of atoms moving with displacements either parallel or perpendicular to the wave vector. Therefore, waves propagating along these directions can be classified as purely longitudinal or transverse. As the transverse waves do not cause local density fluctuations towards the direction of wave propagation, density-density correlation function and the corresponding dynamic structure factor are incapable of revealing information about these modes. Therefore, to identify transverse lattice vibrations, one needs to consider the time-dependent correlations of transverse velocity components.

Adhering to the same nomenclature as before, let us define the microscopic “velocity density” as
\[
\rho_v(r, t) = \sum_i v_i(t) \delta[r - r_i(t)].
\] (3.52)
The corresponding spatial Fourier transform is
\[
\rho_v(q, t) = \sum_i v_i(t) e^{-iq \cdot r_i(t)}.
\] (3.53)
\(\rho_v(q, t)\) can be separated into two components, namely, a longitudinal component which represents the atomic displacements parallel to the wave vector \(q\):
\[
\rho_v^L(q, t) = \sum_i v_i^L(t) e^{-iq \cdot r_i(t)},
\] (3.54)
and a transverse component which represents the displacements perpendicular to the wave vector:
\[
\rho_v^T(q, t) = \sum_i v_i^T(t) e^{-iq \cdot r_i(t)},
\] (3.55)
where \(v_i^L = (v_i \cdot \hat{q}) \hat{q}\), and \(v_i^T = v_i - v_i^L\), with \(\hat{q} = q/|q|\).
Spatial Fourier transforms of the longitudinal and transverse velocity-velocity correlation functions are given by

\[ F_{vv}^{L,T}(q, t) = \frac{1}{N} \langle \rho_{v}^{L,T}(q, t) \cdot \rho_{v}^{L,T}(-q, 0) \rangle , \]  

and the respective power spectrum takes the form

\[ S_{vv}^{L,T}(q, \omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} F_{vv}^{L,T}(q, t) e^{-i\omega t} dt. \]

Peaks in \( S_{vv}^{L}(q, \omega) \) and \( S_{vv}^{T}(q, \omega) \) respectively reveal longitudinal and transverse vibrational modes of the system. It can be shown that \( S_{vv}^{L}(q, \omega) \) is directly related to the density-density dynamic structure factor \( S_{nn}(q, \omega) \) via the relationship [44, 107]

\[ S_{nn}(q, \omega) = \left( \frac{\omega}{q} \right)^2 S_{vv}^{L}(q, \omega). \]  

### 3.8.2 Magnetic excitations

Just as the time-dependent density-density and velocity-velocity correlations reveal vibrational excitations associated with the lattice subsystem, spin density autocorrelations can elucidate the magnetic excitations associated with the spin subsystem.

The microscopic spin density is given by

\[ \rho_{s}(r, t) = \sum_{i} S_{i}(t) \delta(r - r_{i}(t)). \] 

Treating the spin-spin correlations along \( x, y, \) and \( z \) directions separately, we define the intermediate scattering function as

\[ F_{ss}^{k}(q, t) = \frac{1}{N} \langle \rho_{s}^{k}(q, t) \rho_{s}^{k}(-q, 0) \rangle , \] 

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where \( k = x, y, \text{ or } z \), and \( \mathbf{r}_s(t) = \sum_i S_i(t) e^{-i\mathbf{q} \cdot \mathbf{r}_i(t)} \). For a ferromagnetic system in the microcanonical ensemble, the magnetization vector is a constant of motion and serves as a fixed symmetry axis throughout the time evolution of the system. To differentiate between the magnetic excitations that propagate parallel and perpendicular to this symmetry axis, one needs to separately evaluate the respective longitudinal and transverse components of the intermediate scattering function. At the beginning of our microcanonical MD-SD simulations, once the equilibrium initial configuration is generated, we redefine the coordinate system in spin space such that the \( z \) axis is parallel to the magnetization vector. The components \( \{ F^k_{ss}(q, t) \} \) can then be simply regrouped to yield the longitudinal component

\[
F^L_{ss}(q, t) = F^z_{ss}(q, t), \tag{3.61}
\]

and the transverse component

\[
F^T_{ss}(q, t) = \frac{1}{2} (F^x_{ss}(q, t) + F^y_{ss}(q, t)). \tag{3.62}
\]

Note that such regrouping is unnecessary at temperatures above the critical temperature \( T_c \) since all three components \( \{ F^k_{ss}(q, t) \} \) become equivalent due to the spin subsystem being rotationally invariant.

Fourier transforms of \( F^L_{ss}(q, t) \) and \( F^T_{ss}(q, t) \) yield the spin-spin dynamic structure factors

\[
S^{L,T}_{ss}(q, \omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} F^L,T_{ss}(q, t) e^{-i\omega t} dt. \tag{3.63}
\]

Just as the density-density dynamic structure factor, spin-spin dynamic structure factor is a measurable quantity in inelastic neutron scattering experiments [45, 17].
### 3.8.3 Accessible wave vectors

In our simulations, we are primarily interested in investigating the wave propagations in the three principle lattice directions: [100], [110] and [111]. Let us denote the wave vectors along these directions as \( q = (q, 0, 0) \), \( (q, q, 0) \), and \( (q, q, q) \), respectively. Due to the finite size of the simulation box, the accessible values of \( q \) in each direction is constrained to an infinite discrete set:

\[
q = 0, \pm \frac{2\pi}{La}, \pm \frac{4\pi}{La}, \ldots ,
\]

where \( L \) is the linear lattice dimension, and \( a = 2.8665 \text{ Å} \) is the lattice constant of the bcc iron lattice. Moreover, the Brillouin zone boundary in each direction limits the allowed \( q \) values to a finite range, \(-q_{zb} < q < q_{zb}\). Combining these two constraints, we obtain the finite set of accessible \( q \) values in each direction as

\[
q = \begin{cases} 
2\pi n_q / La, & n_q = 0, \pm 1, \pm 2, \ldots, \pm L \quad \text{for } q = (q, 0, 0), (q, q, q) \\
2\pi n_q / La, & n_q = 0, \pm 1, \pm 2, \ldots, \pm L/2 \quad \text{for } q = (q, q, 0)
\end{cases}
\]

### 3.9 Microcanonical MD-SD simulations: An algorithm test

One of the most important decisions regarding atomistic dynamical simulations is the choice of an appropriate time step for the integration algorithm. Typically, a decision on the size of the time step is made by considering the accuracy within which the conservation laws of the dynamics are observed over a period of time. In general, the accuracy can be improved by decreasing the time step, but making it too short will lead to an undesirable increase in the execution time. The ideal choice would be a time step that is short enough to provide an
acceptable accuracy, but not too short that the time integration proceeds at an adequate execution speed.

The equations of motion in the MD-SD formalism as presented in Eqs. (2.36) and (2.37) impose conservation of total energy, and for the special case of constant spin lengths, conservation of magnetization as well. To investigate the effect of the time step size on the preservation of these conservation laws, we perform microcanonical MD-SD simulations on a 16 × 16 × 16 bcc simulation cell (8192 atoms/spins). As for the initial states, the sub-configuration of positions and spins was equilibrated to a temperature of $T = 800$ K using the Metropolis MC method, while the velocities were drawn from the Maxwell-Boltzmann distribution at the same temperature. The equations of motion were integrated up to 1 ns.

For the first set of simulations, we enforce constant spin lengths as given by $S = \frac{\mu_{\text{ground}}}{g\mu_B}$, where $\mu_{\text{ground}} = 2.2\mu_B$ is the atomic magnetic moment observed in the ferromagnetic ground state of bcc iron (See section 2.4.3). Fig. 3.7 shows the total energy per atom as a function of time for different integration time steps. For the larger time steps considered, we observe systematic drifts in the energy. With the smallest time step $\tau = 1$ fs, the energy conservation can be achieved to within six significant digits, without any noticeable drifts (see Fig. 3.8). However, even with $\tau = 1$ fs, we were unable to obtain a reasonable level of precision for the conservation of magnetization (See the green curve in Fig. 3.9). The poor precision in the magnetization conservation is a result of the shorter characteristic time scale associated with the dynamics of spin degrees of freedom in comparison to the translational degrees of freedom. (The difference in the characteristic time scales is corroborated by the relative difference in the frequency range of the lattice vibrations and the transverse spin waves. See chapter for details.) In principle, one can improve the precision of the magnetization conservation by further reducing the integration time step $\tau$, but that would unnecessarily slow down the time integration due to too many time-consuming force-calculations involved. A better solution would be to use the original time step $\tau = 1$ fs for
Figure 3.7: Time evolution of the total energy per atom in microcanonical MD-SD simulations performed on a $16 \times 16 \times 16$ simulation cell. The curves are for different integration time steps $\tau$ and the same initial configuration. Constant spin lengths were enforced.

Figure 3.8: Time evolution of the total energy per atom in a microcanonical MD-SD simulation performed with the integration time step $\tau = 1$ fs, shown on an expanded $y$-axis scale. A $16 \times 16 \times 16$ simulation cell was used. Constant spin lengths were enforced.
the slowly evolving translational degrees of freedom, and adopt a smaller time step $\tau_s$ just for the comparatively faster spin dynamics evolutions. To realize this, we rewrite the spin evolution operator $e^{L_s \tau}$ as

$$e^{L_s \tau} = \left[ e^{L_s \tau_s} \right]^k, \quad \text{where} \quad \tau_s = \tau/k,$$

with $k$ being a positive integer. That is, the single spin dynamics operation $e^{L_s \tau_s} \{s_i\}$ is replaced by a $k$ number of spin dynamics operations that are sequentially performed using a reduced time step of $\tau_s = \tau/k$. Fig. (3.9) shows the time evolution of the magnetization for different values of $\tau_s$. As expected, a decrease in $\tau_s$ considerably reduces the amplitude of the magnetization fluctuations. With $\tau_s = 0.2$ fs ($k = 5$), these fluctuations are reduced by an order of magnitude when compared to the results for $\tau_s = 1$ fs (see Fig. 3.10).

When using the time steps $\tau = 1$ fs and $\tau_s = 0.2$ fs, the deviation in energy ($\sim 0.00001$ eV) that occurs during the 1 ns integration time period is two orders of magnitude smaller than the energy fluctuations ($\sim 0.001$ eV) between the initial states as determined from the standard deviation of 50 independent runs. Similarly, the magnetization deviation ($\sim 0.0002 \mu_B$) during the whole integration process is much smaller than the magnetization fluctuations ($\sim 0.02 \mu_B$) between the initial states. Thus, we believe that the numerical precision in which both energy and magnetization conservation are realized when using these time steps is quite sufficient for our purposes. Therefore, unless specifically stated otherwise, for all the MD-SD simulations discussed in the remainder of thesis, we adopt the time steps $\tau = 1$ fs and $\tau_s = 0.2$ fs.

Now, we allow for the spin lengths to dynamically vary according to the local atomic environment via Eq. (2.55), and investigate its influence on the conservation laws. As shown in Fig. 3.11 (b), introduction of environment-dependent spin lengths does not degrade the precision of the energy conservation. However, since the changes in spin lengths are
Figure 3.9: Time evolution of the net magnetization per atom in microcanonical MD-SD simulations performed on a $16 \times 16 \times 16$ simulation cell. In all simulations, a time step of $\tau = 1$ fs was used for the evolution of translational degrees of freedom, whereas for the spin sub-dynamics, different reduced time steps $\tau_s = \tau/k$ were adopted. Constant spin lengths were enforced.

Figure 3.10: Time evolution of the net magnetization per atom for a microcanonical MD-SD simulation performed with the time steps $\tau = 1$ fs and $\tau_s = 0.2$ fs adopted for atomic evolutions and spin evolutions, respectively. A $16 \times 16 \times 16$ simulation cell was used. Constant spin lengths were enforced.
not derived from the Hamiltonian itself, but are obtained through a mechanism indirectly related to the simulation model, the conservation of magnetization no longer holds. Large fluctuations in the net magnetization ($\sim 10^{-2} \mu_B$) as seen in fig. 3.11 (b) are merely consequences of this artifact, and should not be misinterpreted as numerical errors. Henceforth, unless specifically stated otherwise, for the MD-SD simulations presented in the remainder of this thesis we assume constant spin lengths, $S = \mu_{\text{ground}}/g\mu_B$.

### 3.10 Canonical MD-SD simulations: An algorithm test

As discussed in section 3.7, there are two ways of performing MD-SD simulations in the canonical ensemble:

1. By controlling the lattice temperature via a thermostat coupled to the lattice subsystem

2. By controlling the spin temperature via a thermostat coupled to the spin subsystem

In a physical point of view, the first approach corresponds to an external heat reservoir in contact with the system which exclusively interacts via phonons (e.g. a non-magnetic insulator), whereas the second approach corresponds to a “magnetic” heat bath which only interacts with the spin degrees of freedom (e.g. a thermally insulated paramagnet in the close vicinity of the system). If the coupling between the lattice and the spin subsystem is properly established, controlling the temperature of one of the two subsystems should allow the other subsystem to thermalize towards the same equilibrium temperature.

In what follows, we separately apply these two approaches to a $16 \times 16 \times 16$ coupled spin-lattice system and observe the thermal equilibration process. First, we apply the second approach (i.e. spin thermostat) by adopting the Langevin spin dynamics technique. Initially, all the atoms of the system were arranged on a perfect bcc lattice with spins oriented along the $z$ direction, and velocities set to zero. The target temperature was chosen to be $800 \text{ K}$,
and the damping parameter $\gamma$ of the Langevin spin dynamics equation was set to 0.1. The results of the simulation are summarized in Fig. 3.12, with subset (a) showing the time evolution of the instantaneous lattice and spin temperatures, and subset (b) showing the net magnetization. Both the spin temperature and the magnetization reach their corresponding equilibrium values within a fraction of a picosecond, as the spin subsystem rapidly approaches equilibrium with the coupled magnetic heat bath. As anticipated, the coupling between the lattice and the spin subsystem facilitates the thermalization of atomic degrees of freedom, allowing the lattice temperature to gradually increase and converge to the same equilibrium temperature.

Now, we replace the magnetic heat bath with a phonon heat bath, and repeat the above thermalization procedure. The phonon heat bath was modeled by adopting the Langevin dynamics equation for the translational degrees of freedom, with the damping constant $\eta$ set to 20 ps$^{-1}$. The results are shown in Fig. 3.13. Due to the direct contact with the heat bath, the lattice subsystem rapidly thermalizes and reaches the equilibrium within a fraction of a picosecond. However, the coupling between the lattice and the spin subsystem fails to initiate the thermal excitation of the spin orientations, constraining the spin temperature [subset (a)] and the magnetization [subset (b)] to remain constant throughout the simulation.

The reason behind this anomalous behavior can be explained as follows. In the MD-SD Hamiltonian (2.35), the coupling between the lattice and the spin subsystem is established via the coordinate-dependence of the exchange interaction, which allows the exchange of energy between the two subsystems. However, this exchange coupling does not necessarily facilitate the mutual equilibration between the two subsystems. Due to the rotational symmetry of the Hamiltonian, in the absence of any external torques that explicitly perturb the spin orientations, the total spin angular momentum remains a constant of motion, irrespective of the dynamics of the lattice subsystem. In the case of the phonon heat bath, this unrealistic constraint strictly prohibits the thermalization of the spins and prevents the two subsystems...
from achieving mutual equilibrium. The solution to this issue requires the incorporation of additional spin-lattice interaction terms to the Hamiltonian, which will be the primary focus of chapter 5.
Figure 3.11: Time evolution of the total energy (a) and net magnetization (b) per atom for a microcanonical MD-SD simulation performed with the spin lengths allowed to vary according to the local atomic environment. A $16 \times 16 \times 16$ simulation cell was used.
Figure 3.12: Thermalization of a $16 \times 16 \times 16$ simulation cell with the spin subsystem coupled to a heat bath at the temperature $T = 800$ K. Subset (a) shows the time evolution of the instantaneous lattice temperature ($T_L$) and the spin temperature ($T_S$) while subset (b) shows the magnetization per atom.
Figure 3.13: Thermalization of a 16 × 16 × 16 simulation cell with the lattice subsystem coupled to a heat bath at the temperature $T = 800$ K. Subset (a) shows the time evolution of the instantaneous lattice temperature ($T_L$) and the spin temperature ($T_S$) while subset (b) shows the magnetization per atom.

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Chapter 4

Collective excitations in bcc iron

4.1 Simulation details

To characterize phonon and magnon modes in bcc iron, we performed MD-SD simulations of coupled spin-lattice systems of size \( L = 16 \) at temperatures \( T = 300 \) K and 800 K. The initial states for the time integration were prepared using the procedure described in section 3.6. Equations of motion were integrated up to a total time of \( t_{\text{max}} = 1 \) ns, using the time steps \( \tau = 1 \) fs and \( \tau_s = 0.2 \) fs. Spatial Fourier transforms of the space-displaced, time-displaced correlation functions associated with the density-density, velocity-velocity, and spin-spin correlations were computed “on the fly” for the three principle lattice directions: [100], [110] and [111]. To reduce statistical fluctuations, we have performed a total number of 200 independent simulations for each temperature. The complete set of results was divided into 10 groups of equal size, and the data within each group were averaged over to yield 10 results sets. Dynamic structure factors were independently computed for these 10 correlation function sets, from which we obtain the final average values and the error estimates.

The calculation of dynamic structure factors as given by the Eqs. (3.51), (3.57), and (3.63) involves integrations over \(-\infty < t < +\infty\). In practice, these integrals can only be performed
up to some finite time cutoff $t_{\text{cutoff}}$, which can unfortunately introduce many oscillations into the results [17]. These oscillations can be smoothed out by convoluting the correlation functions with a resolution function in frequency (see Refs. [15, 16] for example). In our case, we used a comparatively longer cutoff time of $t_{\text{cutoff}} = 0.5$ ns, which did not yield any visible oscillations in the dynamic structure factor outside the statistical error bars. Therefore, for the calculations presented in this thesis, we did not use a resolution function.

As our primary goal is to understand the mutual impact of the phonons and magnons on their respective frequency spectra and lifetimes, we have also performed stand-alone MD and SD simulations for comparison. For the MD simulations, we used the Dudarev-Derlet potential to model the interatomic interactions while completely neglecting the spin-spin interactions. The SD simulations were conducted with the atoms frozen at perfect bcc lattice positions, and the exchange parameters determined from the same pairwise function used in MD-SD runs, i.e. Eq. (2.52). The simulation parameters for the stand-alone MD and SD simulations were chosen to be the same as for the MD-SD runs, and the results were analyzed using the same procedure described above.

4.2 Vibrational excitations

For both temperatures $T = 300$ K and $T = 800$ K, we observe well defined excitation peaks at non-zero frequencies in the density-density dynamic structure factor $S_{nn}(q, \omega)$, as well as in the longitudinal and the transverse components of the velocity-velocity dynamic structure factor: $S_{vv}^{L}(q, \omega)$ and $S_{vv}^{T}(q, \omega)$. For each $q$ along [100] and [111] lattice directions, all three quantities show single peaks. Fig. 4.1 shows $S_{nn}(q, \omega), S_{vv}^{L}(q, \omega)$ and $S_{vv}^{T}(q, \omega)$ obtained from our MD-SD simulations at $T = 300$ K for the first five $n_q$ values along the [100] direction. The peak positions in $S_{nn}(q, \omega)$ and $S_{vv}^{L}(q, \omega)$ for the same wave vector coincide with each other as they are both associated with the longitudinal vibrational modes, and hence convey
the same information. The peaks in \( S_{vv}^T(q, \omega) \) are associated with the transverse lattice vibrations. Since there are two orthogonal directions perpendicular to a given wave vector \( q \), there are, in fact, two transverse vibrational modes for each \( q \). Due to the four-fold and three-fold rotational symmetry about the axes \([100]\) and \([111]\), respectively, the two transverse modes for the wave vectors along these directions become degenerate [108]. As a result, we only observe a single peak in \( S_{vv}^T(q, \omega) \) for the wave vectors along these directions.

We also observe single peak structures in \( S_{nn}(q, \omega) \) and \( S_{vv}^L(q, \omega) \) for the wave vectors along the \([110]\) direction. However, for the case of \( S_{vv}^T(q, \omega) \), one can clearly identify two distinct peaks (See Fig. 4.2). This is a consequence of the two transverse modes being non-degenerate due to the reduced rotational symmetry (two-fold) about the \([110]\) axis in comparison to \([100]\) and \([111]\) directions [108].

To extract the positions and the half widths of the phonon peaks, we fit the simulation results for the dynamic structure factor to a Lorentzian function of the form [20, 21]

\[
S(q, \omega) = \frac{I_0 \Gamma^2}{(\omega - \omega_0)^2 + \Gamma^2},
\]

where \( \omega_0 \) is the characteristic frequency of the vibrational mode, \( I_0 \) is the intensity or the amplitude of the peak, and \( \Gamma \) is the half width at half maximum (HWHM) which is inversely proportional to the lifetime of the excitation. For both \( T = 300 \text{ K} \) and \( T = 800 \text{ K} \), and for all wave vectors considered, Lorentzian lineshape given in Eq. (4.1) fit well with the peaks observed in \( S_{nn}(q, \omega) \) and \( S_{vv}^L(q, \omega) \). Fig. 4.3 shows an example curve fit for the MD-SD results of \( S_{nn}(q, \omega) \) for \( q = (1.1 \text{ Å}^{-1}, 0, 0) \) at \( T = 300 \text{ K} \). To estimate the errors in the fitting parameters, we separately fitted Lorentzians to the 10 independent dynamic structure factor estimates described in section 4.1. The standard deviations of the fitting parameters obtained from the 10 independent curve fits were found to be larger than the errors estimated by the
Figure 4.1: The density-density dynamic structure factors [subset (a)], and the longitudinal [subset (b)] and the transverse [subset (c)] components of the velocity-velocity dynamic structure factors obtained from MD-SD simulations for the first five $n_q$ values along the [100] direction. The simulations were performed for $L = 16$ at $T = 300$ K. The inset of (b) shows an expanded view of the peak in $S^L_{vv}(q, \omega)$ for $n_q = 1$ with error bars.
Figure 4.2: The transverse components of the velocity-velocity dynamic structure factors obtained from MD-SD simulations for the first three $n_q$ values along the [1 1 0] direction for $L = 16$ at $T = 300$ K.

Figure 4.3: Fitting a Lorentzian lineshape of the form Eq. (4.1) for the density-density dynamic structure factor for $\mathbf{q} = (1.1 \, \text{Å}^{-1}, 0, 0)$ obtained from MD-SD simulations for $L = 16$ at $T = 300$ K.
curve-fitting tool for all cases. Therefore, we chose the aforementioned standard deviations as the errors in the fitting parameters. To fit the two peak structure observed in $S^T_{vv}(q, \omega)$ for the [110] direction, we use the sum of two Lorentzians with different sets of fitting parameters.

Using the peak positions obtained from the Lorentzian fits, one can construct phonon dispersion relations for the three principle lattice directions. Fig. 4.4 shows the the dispersion curves determined from our MD-SD simulations for $T = 300$ K, along with the experimental results [109, 110] obtained from inelastic neutron scattering. For comparison, we have also shown the results of stand-alone MD simulations for the same temperature. In general, for small to moderate $q$ values, both MD-SD and MD dispersion curves agree well with the experimental results, but deviations can be observed for larger $q$ values, particularly near the zone boundaries in [100] and [111] directions. Although the MD-SD and MD dispersion curves are indistinguishable within the resolution of Fig. 4.4, we will later on show that there are, in fact, deviations larger than the statistical errors. Fig. 4.5 compares the MD-SD dispersion curves for $T = 300$ K and $T = 800$ K. The MD results for $T = 800$ K are also shown, but one cannot observe any significant difference between the MD-SD and MD dispersion curves within the resolution of the figure. The characteristic phonon frequencies for all branches seem to decrease as the temperature is increased, an effect which is particularly evident for larger $q$ values.

At temperatures in the vicinity of absolute zero, due to the low occupation of vibrational modes, phonons behave as weakly interacting quasiparticles that can be treated within the harmonic approximation [111]. In this limit, characteristic frequencies of the phonons are well defined and the lifetimes are practically infinite. As the temperature is increased, phonon occupation numbers also increase, which in turn increases the probability of mutual interactions. As a result of such phonon-phonon scattering at elevated temperatures, characteristic frequencies of the phonons may shift, and the lifetimes may shorten [111, 112]. (In fact, the temperature-induced softening of phonons as observed in Fig. 4.5 is a consequence of
Figure 4.4: Comparison of the phonon dispersion curves obtained from MD-SD simulations ($L = 16$) with the experimental results [109, 110] for $T = 300$ K. Results obtained from pure MD simulations are also plotted for comparison. LA and TA, respectively, denote the longitudinal and transverse branches.

Figure 4.5: Comparison of the phonon dispersion curves for $T = 300$ K and $T = 800$ K obtained from MD-SD simulations for $L = 16$. Results for $T = 800$ K obtained from pure MD simulations are also shown.
increased phonon-phonon scattering at high temperatures.) In magnetic crystals, the co-
existence of phonons and magnons gives rise to another class of scattering processes, namely, phonon-magnon scattering. Just as phonon-phonon scattering, phonon-magnon scattering may also lead to a shift in the characteristic phonon frequencies, as well as shortening of the phonon lifetimes. As the occupancy of both phonon and magnon modes increases with temperature, these effects will be more pronounced as the temperature is increased.

To carefully examine the changes in the phonon frequency spectrum due to magnons, we compare the characteristic frequencies determined from MD-SD simulations ($\omega_{\text{MD-SD}}$) with the ones obtained from MD simulations ($\omega_{\text{MD}}$) by calculating the fractional frequency shift, $(\omega_{\text{MD-SD}} - \omega_{\text{MD}})/\omega_{\text{MD}}$. The results for the three principle directions are shown in Figs. 4.6 and 4.7, for the longitudinal and the transverse modes, respectively. With the exception of the high frequency transverse branch along [110] direction (TA2), phonon frequencies shift to higher values in the presence of magnons. In general, the shift in frequencies becomes more pronounced as the temperature is increased. A particularly interesting behavior occurs in the longitudinal branch for the [111] direction where we observe dips in the curves for both $T = 300\ K$ and $T = 800\ K$ at the same $q$ value. For both temperatures, the frequency shift of the vibrational mode that corresponds to the bottom of the dip is close to zero. Therefore, the frequency of this phonon mode appears to be unaffected by the presence of magnons at both temperatures.

Lifetimes of the phonon excitations are inversely proportional to the half widths at half maximum of the corresponding vibrational peaks observed in $S_{nn}(\mathbf{q},\omega)$ and $S^{L,T}_{vv}(\mathbf{q},\omega)$. To study the impact of the magnons on the phonon lifetimes, we compare the half widths obtained from MD-SD simulations with that of the MD simulations. Fig. 4.8 and Fig. 4.9, respectively, show the results for the longitudinal and transverse phonons. For the longitudinal phonons at $T = 300\ K$, a marginal increase in the half widths can be observed due to the magnons, which becomes more pronounced as the temperature is increased to 800 K.
Figure 4.6: The fractional shift in longitudinal phonon frequencies due to magnons for $L = 16$ at $T = 300$ K and $T = 800$ K in the (a) [1 0 0], (b) [1 1 0], and (c) [1 1 1] lattice directions.
Figure 4.7: The fractional shift in transverse phonon frequencies due to magnons for \( L = 16 \) at \( T = 300 \) K and \( T = 800 \) K in the (a) [1 0 0], (b) [1 1 0], and (c) [1 1 1] lattice directions.
Figure 4.8: Half width at half maximum (HWHM) of the longitudinal phonons at $T = 300$ K and $T = 800$ K obtained from MD-SD and MD simulations for $L = 16$ in the (a) $[100]$, (b) $[110]$, and (c) $[111]$ lattice directions.
Figure 4.9: Half width at half maximum (HWHM) of the transverse phonons at $T = 300$ K and $T = 800$ K obtained from MD-SD and MD simulations for $L = 16$ in the (a) $[100]$, (b) $[110]$, and (c) $[111]$ lattice directions.
For the case of transverse phonons, the increase in half width due to magnons is negligible when compared to that of the longitudinal phonons. At \( T = 300 \text{ K} \), we do not observe any difference between the MD-SD and MD results outside the error bars. At \( T = 800 \text{ K} \), a marginal increase can be observed, especially for the [111] direction.

### 4.3 Magnetic excitations

#### 4.3.1 Transverse magnon modes

For both temperatures \( T = 300 \text{ K} \) and \( T = 800 \text{ K} \), our results for the transverse component of the spin-spin dynamic structure factor \( S_{ss}^T(q, \omega) \) show a single spin wave peak. Fig. 4.10 shows \( S_{ss}^T(q, \omega) \) obtained from MD-SD simulations for \( L = 16 \) at \( T = 300 \text{ K} \) for the first five \( n_q \) values along the [100] direction. For \( T = 300 \text{ K} \), the single spin-wave peaks obtained from both MD-SD and SD simulations fit well to Lorentzian lineshapes of the form Eq. (4.1). For the case of MD-SD results at \( T = 800 \text{ K} \), especially for large values of \( q \), the peaks are asymmetric, and hence do not yield good fits to Lorenzian lineshapes. Therefore, one cannot obtain reliable estimates of the magnon half widths for the MD-SD results at \( T = 800 \text{ K} \). However, the spin wave peak positions can still be determined relatively accurately, thus the magnon dispersion relations can be constructed.

Fig. 4.11 shows the transverse magnon dispersion relations for small \(|q|\) values along the three principle directions as determined from MD-SD simulations at \( T = 300 \text{ K} \). In agreement with the experimental findings [113, 114], the three dispersion relations are isotropic when plotted as functions of the magnitude of the wave vector \(|q|\). Moreover, for small \(|q|\) values, our results agree quantitatively with the experimental results for the [110] direction [113, 114]. Fig. 4.12 shows the complete dispersion curves determined from MD-SD and SD simulations for \( T = 300 \text{ K} \) and \( T = 800 \text{ K} \). For both MD-SD and SD, the characteristic frequencies shift to lower values as the temperature is increased from 300 K to 800 K. This indicates increased
The transverse components of the spin-spin dynamic structure factors obtained from MD-SD simulations for the first five $n_q$ values along the [100] direction for $L = 16$ at $T = 300$ K. The inset shows an expanded view of the last three peaks ($n_q = 3, 4, 5$) which are not discernible in the main figure.

Magnon-magnon scattering at elevated temperatures. For both temperatures, particularly near the zone boundaries, we can observe a marginal difference between the MD-SD and SD dispersion curves. This, in fact, is a result of phonon-magnon scattering.

To further investigate the magnon softening due to phonons, we calculate the fractional frequency shift of the magnons, $(\omega_{\text{MD-SD}} - \omega_{\text{SD}}) / \omega_{\text{SD}}$. The results are shown in Fig. 4.13 for the three principle directions. For small $q$ values, magnon modes shift to lower frequencies in the presence of phonons. As $q$ increases, the direction of the shift is reversed. Moreover, the shift in frequencies becomes more pronounced as the temperature is increased from 300 K to 800 K.

Fig. 4.14 compares the transverse magnon half widths obtained from MD-SD and SD simulations for $T = 300$ K. Although the difference between the half widths is negligible
Figure 4.11: Transverse magnon dispersion relations at $T = 300$ K obtained from MD-SD simulations for $L = 16$. The experimental results reported by Lynn [113] and Collins [114] for the [1 1 0] direction are also plotted for comparison.

Figure 4.12: Transverse magnon dispersion curves for $T = 300$ K and $T = 800$ K obtained from MD-SD and SD simulations for $L = 16$. 

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Figure 4.13: The fractional shift in transverse magnon frequencies due to phonons for $L = 16$ at $T = 300$ K and $T = 800$ K in the (a) [1 0 0], (b) [1 1 0], and (c) [1 1 1] lattice directions.
Figure 4.14: Half width at half maximum (HWHM) of the transverse magnons at $T = 300$ K obtained from MD-SD and SD simulations for $L = 16$ in the (a) [1 0 0], (b) [1 1 0], and (c) [1 1 1] lattice directions.
for small $q$ values, for moderate to large $q$ values, half widths for the MD-SD results are significantly larger than that for the SD results. This indicates significant shortening of the magnon lifetimes due to phonon-magnon scattering.

### 4.3.2 Longitudinal magnetic excitations

Our results for the longitudinal spin-spin dynamic structure factor $S_{ss}^{L}(q, \omega)$ obtained from both MD-SD and SD simulations show many very low-intensity excitations peaks, for all wave vectors considered. Fig. 4.15 shows $S_{ss}^{L}(q, \omega)$ for a small system size $L = 8$ at $T = 300$ K, where we compare the SD results [subset (a)] with the MD-SD results [subset (b)] for $q = \frac{2\pi}{L_a}(1, 0, 0)$.

In the context of classical Heisenberg models, Bunker et al. [18] showed that the excitation peaks observed in $S_{ss}^{L}(q, \omega)$ are two-spin-wave creation and/or annihilation peaks which result from the pairwise interactions between transverse magnon modes. For ferromagnetic systems, only spin wave annihilation peaks are present, and their frequencies are given by

$$
\omega_{ij}^{-}(q_i \pm q_j) = \omega(q_i) - \omega(q_j),
$$

(4.2)

where $q_i$ and $q_j$ are the wave vectors of the two transverse magnon modes which comprise the two-spin-wave excitation. Since the set of allowable wave vectors $\{q_i\}$ depends on the system size $L$, the resultant two-spin-wave spectrum also varies with $L$. For a real magnetic crystal where $L$ is practically infinite, the two-spin-wave spectrum would become continuous.

To verify whether the peaks we observe in $S_{ss}^{L}(q, \omega)$ are two-spin-wave peaks, we chose a relatively small system size ($L = 8$) so that the set of allowable wave vectors is reduced to a manageable size. Then, using MD-SD and SD simulations, we separately determined the transverse magnon frequencies that correspond to the first few $n_q$ values along all possible lattice directions. With this information at hand, we can predict the expected positions of
Figure 4.15: The longitudinal component of the spin-spin dynamic structure factor $S_{ss}^L(q, \omega)$ for $q = \frac{2\pi}{L}(1, 0, 0)$ obtained from (a) SD and (b) MD-SD simulations for $L = 8$ at $T = 300$ K. The predicted positions of the two-spin-wave annihilation peaks are indicated by black dashed lines. The label attached to each line shows the two single spin wave modes responsible for the annihilation peak. The red dotted line [LA (100)] marks the frequency of the longitudinal phonon mode for the same $q$. 

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all the two-spin-wave annihilation peaks using Eq. (4.2) for both SD and MD-SD case. As an example, let us consider the wave vector pair \( \mathbf{q}_i = (1, 1, 1) \) and \( \mathbf{q}_j = (1, 1, 0) \). Since \( \mathbf{q}_i - \mathbf{q}_j = (0, 0, 1) \), they produce a spin wave annihilation peak in \( S_{ss}^L(\mathbf{q}, \omega) \) for \( \mathbf{q} = (0, 0, 1) \) at the frequency \( \omega^- = \omega(\mathbf{q}_i) - \omega(\mathbf{q}_j) \). (Note that we have ignored the common pre-factor \( 2\pi/La \) from the wave vectors.)

In Fig. 4.15 (a) and (b), we have superimposed the predicted spin wave annihilation peak positions corresponding to each case. We see an excellent match between the observed peaks and the predicted two-spin-wave peak positions, with the exception of the particular sharp peak at \( \omega \approx 10 \text{ meV} \) which only appears in subset (b). Surprisingly, the position of this peak coincides with the frequency of the longitudinal phonon mode for the same \( \mathbf{q} \) as determined from the peak position of \( S_{nn}(\mathbf{q}, \omega) \) or \( S_{vv}^L(\mathbf{q}, \omega) \). Similar excitation peaks were observed for all wave vectors, for all system sizes and temperatures considered. We conjecture that these peaks represent propagating longitudinal spin wave excitations that are coupled with longitudinal lattice vibrations of the same frequency. Existence of such coupled phonon-magnon modes is a new phenomenon that so far hasn’t been discovered experimentally. In fact, this is not surprising since the experimental detection of these peaks would be extremely challenging due to their very low intensities.

### 4.4 Calculations with Finnis-Sinclair potential

During the preliminary stages of our work on MD-SD, we used the Finnis-Sinclair (FS) potential to model the interatomic interactions. Since the Dudarev-Derlet (DD) potential is known to provide more accurate predictions of the structural and mechanical properties of bcc iron especially for moderate to high temperatures [73, 74], later on, we switched to using the DD potential. In this section, we present some of our earlier work involving the
FS potential. For these calculations, we have allowed the magnetic moments to dynamically vary according to the Voronoi volume of the atoms using Eq. (2.56).

Fig. 4.16 shows the longitudinal phonon dispersion relation for [100] direction obtained from the MD-SD simulations using the FS potential for \( L = 10 \) at \( T = 300 \) K. For comparison, we have also shown the results obtained using the DD potential for the same system size. For the simulations using the DD potential, we allowed the moments to dynamically adjust according to Eq. (2.55). For small \(|q|\), the difference between the dispersion curves is negligible, but significant deviations can be observed for large \(|q|\) values, especially near the zone boundary.

Fig. 4.17 shows the transverse magnon dispersion relations for [100] direction obtained from MD-SD simulations using the FS and DD potentials for \( L = 10 \) at \( T = 300 \) K. The difference between the two dispersion curves increases as \(|q|\) increases. For all wave vectors, the magnon frequencies obtained for the case of the DD potential are higher than the ones obtained for the FS potential. We speculate that this frequency shift is largely due to the fact that two different regression relationships (Eqs. 2.55 and 2.56) are used for predicting the local environment-dependence of the magnetic moments. For the ground state bcc crystal structure, the moment magnitude predicted by Eq. 2.55 (\( \mu_{\text{ground}} \approx 2.16 \)) is smaller than the value predicted by Eq. 2.56 (\( \mu_{\text{ground}} \approx 2.33 \)). Thus, the average spin length in MD-SD simulations using the DD potential is smaller than that for the FS potential. According to Eqs. (2.37) and (2.53), the speed of the precessional motion of a spin is inversely proportional to its magnitude. Hence, one would expect the magnon frequencies obtained for the DD potential to be higher than that for the FS potential.

Just as with the DD potential, we also observe coupled phonon-magnon peaks in \( S^{L}_{ss}(q, \omega) \) for the case of the FS potential. In Fig. 4.18, we compare \( S^{L}_{ss}(q, \omega) \) obtained from MD-SD simulations with the results obtained from SD simulations for the wave vector \( q = \frac{2\pi}{La}(1, 0, 0) \) at \( T = 800 \) K. The sharp peak at \( \omega \approx 7.5 \) meV which only appears in the MD-SD case.
Figure 4.16: Dispersion curves for the longitudinal phonon branch in [100] direction obtained from MD-SD simulations for $L = 10$ at $T = 300$ K using Finnis-Sinclair (FS) and Dudarev-Derlet (DD) potentials. The error bars are smaller than the size of the symbols.

Figure 4.17: Transverse magnon dispersion curves for the [100] direction obtained from MD-SD simulations for $L = 10$ at $T = 300$ K using Finnis-Sinclair (FS) and Dudarev-Derlet (DD) potentials. The error bars are smaller than the size of the symbols.
Figure 4.18: The longitudinal component of the spin-spin dynamic structure factor $S^L_{ss}(q, \omega)$ for $q = \frac{2\pi}{La}(1,0,0)$ obtained from (a) SD and (b) MD-SD simulations for $L = 10$ at $T = 800$ K. For the MD-SD simulations, Finnis-Sinclair potential was used. The red dotted line [LA (100)] marks the frequency of the longitudinal phonon mode for the same $q$. 

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coincides with the frequency of the longitudinal phonon mode for the same \( \mathbf{q} \) as determined from the peak position in \( S_{nn}(\mathbf{q}, \omega) \). Note that in Fig. 4.18, we do not observe as many spin wave annihilation peaks as we observed in Fig. 4.15. The main reason is that the results shown in Fig. 4.18 are for a much higher temperature, thus the intensity of the two-spin-wave peaks has further reduced due to damping, resulting in a much smoother spectrum.
Chapter 5

Incorporating spin-orbit interactions into combined molecular and spin dynamics

5.1 The “missing ingredient” in MD-SD

As discussed in section 3.10, the MD-SD formalism suffers from a fundamental flaw that leads to an inaccurate depiction of the spin-lattice relaxation process. Due to the isotropic nature of the spin-lattice interaction terms in the Hamiltonian, unless the spin orientations are explicitly controlled via external torques, the total vector sum of spins remains a conserved quantity. In the case of non-equilibrium simulations, this constraint imposes an artificial entropic barrier between the lattice and the spin subsystems, and prevents them from achieving mutual equilibrium.

This undesirable feature promotes the need for exploring missing contributions to spin-lattice coupling; when combined with the existing exchange interaction term; that may potentially capture the true dynamics of the relaxation process. An important interaction
currently excluded from MD-SD is spin-orbit (SO) coupling, which serves as a direct channel for the flow of energy and angular momentum between the spins and the lattice in real magnetic crystals [6]. However, in the bulk phase of 3d cubic transition metals and alloys, crystal-field splitting largely suppresses SO interactions [5, 115], leading to coupling strengths that are several orders of magnitude smaller in comparison to the exchange interaction [6]. Nevertheless, in low symmetry environments such as surfaces and thin films, SO coupling is considerably strengthened due to the changes in the periodic potential experienced by the electrons [116, 117]. Following the same argument, we assert that the momentary symmetry breaking of the crystal structure that occurs due to lattice vibrations may substantially enhance SO interactions. This, in turn, may significantly influence the spin-lattice relaxation process at elevated temperatures.

We infer that the critical “missing ingredient” in MD-SD is in fact a classical model that encapsulates such local fluctuations in the SO interactions. Since the notion of orbital angular momentum (L) does not exist in the MD-SD formulation, one cannot introduce SO interactions directly into the Hamiltonian as an atomistic level abstraction of the form, $\mathcal{H}_{SO} \sim L \cdot S$. Therefore, we model the effect of SO coupling via one of its emergent properties, magnetocrystalline anisotropy [118, 119]. As the effective size and the orientational preference of the SO interaction depends on the symmetry of the surrounding atomic environment, the resultant anisotropies will also vary across different atomic sites. Magnitudes and the easy axes of these “induced” local anisotropies will change dynamically as the local environment is continuously distorted by the propagating phonons.
5.2 A phenomenological model for spin-orbit interactions

Henceforth, we will neglect any “background” anisotropy that already resides in the perfect crystalline symmetry, and only focus on the aforementioned induced anisotropies. Based on the first and the second order terms of the anisotropy energy expansion for a single spin, we propose the following terms for the anisotropic components of the Hamiltonian:

\[ H_{\text{anis}} = -C_1 \sum_{i=1}^{N} K_i \cdot S_i - C_2 \sum_{i=1}^{N} S_i^\top \cdot \Lambda_i \cdot S_i, \quad (5.1) \]

where \( C_1 \) and \( C_2 \) are constants, and vector \( K_i \) and tensor \( \Lambda_i \) are variable quantities that define the easy axes and the coupling strengths of the on-site magnetic anisotropy at a given time. \( K_i \) and \( \Lambda_i \) are solely determined by the symmetry of the local atomic environment, and will vanish for perfect cubic crystalline symmetry. In order to establish the connection to the local environment, we write vector \( K_i \) and tensor \( \Lambda_i \) as

\[
K_i = \nabla_{r_i} \varrho_i, \quad \Lambda_i = \begin{pmatrix}
\frac{\partial^2 \varrho_i}{\partial x_i^2} & \frac{\partial^2 \varrho_i}{\partial x_i \partial y_i} & \frac{\partial^2 \varrho_i}{\partial x_i \partial z_i} \\
\frac{\partial^2 \varrho_i}{\partial y_i \partial x_i} & \frac{\partial^2 \varrho_i}{\partial y_i^2} & \frac{\partial^2 \varrho_i}{\partial y_i \partial z_i} \\
\frac{\partial^2 \varrho_i}{\partial z_i \partial x_i} & \frac{\partial^2 \varrho_i}{\partial z_i \partial y_i} & \frac{\partial^2 \varrho_i}{\partial z_i^2}
\end{pmatrix}, \quad (5.2)
\]

where \( \varrho_i(\{r_k\}) \) is a scalar function that quantitatively reflects the local symmetry surrounding the \( i \)th atom. The particular functional form of \( \varrho_i(\{r_k\}) \) will depend on the details of the electronic structure of the material. Since the first principles based formulation of \( \varrho_i(\{r_k\}) \) is beyond the capabilities of the current \textit{ab initio} methods, we phenomenologically construct
\( \varrho_i(\{r_k\}) \) as

\[
\varrho_i = \sum_{j\,(j \neq i)} \phi(r_{ij}),
\]

where \( \phi(r_{ij}) \) is an arbitrary pairwise function. The chosen functional form assures that in perfect cubic crystalline symmetry, \( \nabla_r \varrho_i \) and the off-diagonal elements of \( \Lambda_i \) vanish. While the diagonal elements of \( \Lambda_i \) do not vanish, they become identical, which only contributes to a constant shift in the ground state energy.

For \( \phi(r_{ij}) \), we choose a short-range function

\[
\phi(r_{ij}) = (1 - r_{ij}/r_c)^4 \exp(1 - r_{ij}/r_c) \Theta(r_c - r_{ij})
\]

with the cut-off distance \( r_c = 3.5 \text{ Å} \) between the second and the third nearest neighbor distances of the bcc iron lattice. The fourth-order polynomial component ensures that all interatomic forces due to the coordinate-dependence of \( H_{\text{ani}} \) smoothly approach zero at \( r_c \).

First principles methods such as Locally Self Consistent Multiple Scattering (LSMS) [75] can routinely provide SO energies associated with the vibrational breaking of local symmetry and hence, in principle, estimates for the coefficients \( C_1 \) and \( C_2 \). An attempt at parameterizing \( C_1 \) based on LSMS calculations [120] of a 128 atom configuration with thermal displacements yielded an average value in the order of \( 10^{-1} \text{ eV} \), with a site-to-site root-mean-square deviation of the same order. Such variation from site-to-site demonstrates the difficulty in extracting models for SO energies from the overall energy shifts associated with the local displacements as predicted by LSMS. Therefore, in what follows, we choose values for \( C_1 \) and \( C_2 \) of the order of \( 10^{-1} \text{ eV} \), and further explore the sensitivity of the results to their variations.
5.3 An iterative integration scheme for treating the second order anisotropy term

With the inclusion of the anisotropy terms in Eq. (5.1), the total force \( f_i = -\nabla_r H \) and the effective field \( H_i^{\text{eff}} = -\nabla S_i H \) acting on each atom are respectively modified.

The contribution to the effective field from the first-order term \( H^{(1)} = -C_1 \sum_j \nabla_{r_j} \varrho_j \) is

\[
H_i^{(1)} = -\nabla S_i H_i^{(1)} = C_1 \nabla_{r_i} \varrho_i. \tag{5.5}
\]

The components of the effective field due to off-diagonal elements of the second-order term: \( H_{\alpha \beta}^{(2)} = -C_2 \sum_j \frac{\partial^2 \varrho_j}{\partial \alpha_i \partial \beta_j} S_{j \alpha} S_{j \beta} \) take the form

\[
H_{\alpha \beta}^{(2)} = -\nabla S_i H_{\alpha \beta}^{(2)} = C_2 \frac{\partial^2 \varrho_i}{\partial \alpha_i \partial \beta_i} \left( S_{i \beta} \hat{\alpha} + S_{i \alpha} \hat{\beta} \right), \tag{5.6}
\]

and the components due to diagonal elements \( H_{\alpha \alpha}^{(2)} = -C_2 \sum_j \frac{\partial^2 \varrho_j}{\partial \alpha_j^2} S_{j \alpha}^2 \) are given by

\[
H_{\alpha \alpha}^{(2)} = -\nabla S_i H_{\alpha \alpha}^{(2)} = 2C_2 \frac{\partial^2 \varrho_i}{\partial \alpha_i^2} S_{i \alpha} \hat{\alpha}, \tag{5.7}
\]

where \( \alpha, \beta = x, y, z \). In contrast to the first-order term, the field components due to the second-order term render the spin dynamics equation nonlinear. Thus, the analytical solution for the rotation operation \( e^{i s_i \cdot \hat{S}} S_i \) as given by Eq. (3.26) is no longer applicable. Although it is possible to find an analytical form also for the nonlinear case in terms of Jacobi elliptic functions [24], such solution would involve highly precision sensitive operations and would significantly degrade the performance of the integration algorithm. A more efficient and convenient strategy is to adopt a simple iterative method [24], which can be described as follows.
Consider a single spin evolution step $e^{i\hat{L}_i\tau}S_i(t)$ in the ST sequence (3.25). Let $H_i$ denote the contribution to the total field from all interaction terms that are of first order in $S_i$ (i.e. the exchange interaction and the first order anisotropy). According to the ST formulation, during the operation $e^{i\hat{L}_i\tau}S_i(t)$, all the atomic coordinates and the the spins (excluding $S_i$) are considered to be frozen. Therefore, $H_i$ will essentially remain a constant, while the field due to the second-order term can be regarded as a function of the Cartesian components of $S_i(t)$, i.e. $H_i^{(2)}(t) = H_i^{(2)}(\{S_{i\alpha}(t)\})$, where $\alpha = x, y, z$. The requirement for energy conservation during the operation $e^{i\hat{L}_i\tau}S_i(t)$ yields

$$H_i \cdot S_i(t + \tau) - S_i(t + \tau)^T \cdot \Lambda_i \cdot S_i(t + \tau) = H_i \cdot S_i(t) - S_i(t)^T \cdot \Lambda_i \cdot S_i(t). \quad (5.8)$$

If one can find a transformation $H_i \rightarrow \tilde{H}_i$ such that $\tilde{H}_i \cdot S_i(t + \tau) = \tilde{H}_i \cdot S_i(t)$, then the operation $e^{i\hat{L}_i\tau}S_i(t)$ can be performed as a rotation around the effective rotation axis $\tilde{H}_i$ using Eq. (3.26). It can be shown that such a transformation can indeed be realized as

$$\tilde{H}_i = H_i - \frac{1}{2} \left[ H_i^{(2)}(\{S_{i\alpha}(t)\}) + H_i^{(2)}(\{S_{i\alpha}(t + \tau)\}) \right]. \quad (5.9)$$

Unfortunately, Eq. (5.9) requires $S_i(t + \tau)$ to be known in advance. This problem can be solved by iteratively performing several spin rotations according to Eq. (3.26), starting from an initial guess $S_i(t + \tau) = S_i(t)$.

Unlike in the case of the conventional ST method, with the above iterative method the energy can no longer be conserved exactly during the spin dynamics evolutions. The accuracy of the energy conservation can be improved by increasing the number of iterations, which, in turn, would unfortunately slow down the time integration. Therefore, one should choose an appropriate value that balances the trade-off between the accuracy and the efficiency.
5.4 Results

5.4.1 Performance of the integration scheme

To find the optimal number of iterations and an appropriate integration time step, we carried out a series of pure SD and MD-SD simulations on a $16 \times 16 \times 16$ simulation cell, with the anisotropy coefficients $C_1$ and $C_2$ set to 0.2 eV and 0.1 eV, respectively. As for the initial states, the sub-configuration of positions and spins was equilibrated to a temperature of $T = 800$ K using the Metropolis method, while the velocities were drawn from the Maxwell-Boltzmann distribution at the same temperature. To determine the optimal number of iterations to be used, we first froze the atoms and performed pure SD simulations on the spatially disordered spin configurations using the time step $\tau_s = 0.2$ fs. We found that 3 iterations are sufficient to maintain the energy conserved to within 6 significant digits over time periods up to 1 ns. Then, using 3 iterations per spin dynamics step, we performed MD-SD simulations starting from the same initial states. Fig. 5.1 shows the time evolution of the total energy per atom obtained using the original time step pair used in the isotropic case (i.e. $\tau = 1$ fs, $\tau_s = 0.2$ fs), as well as a reduced time step pair: $\tau = 0.1$ fs, $\tau_s = 0.1$ fs. Unfortunately, the introduction of the spin-orbit terms significantly reduces the quality of energy conservation in MD-SD simulations. The original time step $\tau = 1$ fs is clearly insufficient for achieving a reasonable level of accuracy. Thus, we decided to use the reduced time step pair: $\tau = 0.1$ fs, $\tau_s = 0.1$ fs, which reduces the drift in energy down to $\sim 0.0004$ eV over the 1 ns time period (See Fig. 5.2).

5.4.2 Thermalization via a phonon heat bath

To show that our refined MD-SD model eradicates the shortcomings of the original approach, we repeat the thermalization procedure described in section 3.10 by coupling a phonon heat bath to the lattice subsystem. The anisotropy coefficients $C_1$ and $C_2$ were set to 0.2 eV and
Figure 5.1: Time evolution of the total energy per atom in microcanonical MD-SD simulations enhanced with SO coupling. The curves are for different integration time steps and the same initial configuration. The anisotropy coefficients $C_1$ and $C_2$ were set to 0.2 eV and 0.1 eV, respectively. A $16 \times 16 \times 16$ simulation cell was used.

Figure 5.2: Time evolution of the total energy per atom in a microcanonical MD-SD simulation performed with the integration time step pair: $\tau = 0.1$ fs, $\tau_s = 0.1$ fs. The anisotropy coefficients $C_1$ and $C_2$ were set to 0.2 eV and 0.1 eV, respectively. A $16 \times 16 \times 16$ simulation cell was used.
0.1 eV, respectively. Figs. 5.3 and 5.4 summarize the results for the target temperatures $T = 300$ K and $T = 800$ K, respectively, with the upper panels showing the time evolution of the instantaneous lattice and spin temperatures, and the lower panels showing the net magnetization. As anticipated, the anisotropy terms facilitate the thermalization of the spin orientations, allowing the spin temperature/magnetization to increase/decrease with time. The precessional damping of the spins continues until the coupled spin-lattice system; as a whole; approaches equilibrium with the phonon heat bath. Moreover, a comparison between the Figs. 5.3 and 5.4 shows that the spin relaxation rate increases noticeably with the target temperature. As the temperature of the heat bath increases, thermal fluctuations of the atomic positions also increase. This would further intensity the locally induced anisotropies, leading to an increase in the spin relaxation rate.

### 5.4.3 Sensitivity of the spin relaxation rate to the anisotropy coefficients

With the pairwise function $\phi(r_{ij})$ fixed, the anisotropy coefficients $C_1$ and $C_2$ fully determine the strength of the induced local anisotropies. Changing these coefficients consequently broadens or narrows the SO channel, thereby controlling the relaxation rate of the spin subsystem. To study this effect, we repeat our familiar thermalization procedure for different anisotropy coefficients. Fig. 5.5 (a) shows the results for varying $C_1$ while $C_2$ set to zero, whereas in Fig. 5.5 (b), $C_2$ is varied while $C_1$ held constant at 0.2 eV. For the results shown in Fig. 5.6, $C_1$ is set to zero while $C_2$ is varied. As either of the coefficients is increased, we observe a systematic increase in the spin relaxation rate, which subsequently allows the spin subsystem to reach equilibrium faster. The stability of our model over such a range of coefficients promotes its applicability to a wide class of systems with varying SO coupling strengths. If the interest lies in obtaining realistic relaxation times for the material under
investigation, one can tune $C_1$ and $C_2$ appropriately in accordance with the spin relaxation data obtained through pump-probe experiments [121].

5.4.4 Effect of crystallographic defects on the spin relaxation rate

So far, our discussion on induced anistropies was centered on lattice vibrations as the primary source of symmetry breaking in the local environment. Another source of symmetry breaking that commonly occurs in real crystals is the presence of crystallographic defects. Due to the distortions in the crystal structure surrounding the defect, SO interactions associated with the nearby atoms will be enhanced significantly [122, 123]. As a result, the occurrences of defects in the crystal may have a noticeable impact on the overall spin-lattice relaxation. To investigate this phenomenon, we introduce vacancies into the bcc lattice and perform MD-SD simulations with the lattice subsystem coupled to a phonon heat bath. Fig. 5.7 shows the time evolution of the spin temperature under varying vacancy concentrations. As expected, the relaxation rate of the spin subsystem notably increases as the vacancy concentration is increased.
Figure 5.3: Thermalization of a $16 \times 16 \times 16$ simulation cell with the lattice subsystem coupled to a Langevin heat bath at the temperature $T = 300$ K. Subset (a) shows the time evolution of the lattice and the spin temperatures while subset (b) shows the magnetization per atom. The anisotropy coefficients $C_1$ and $C_2$ were set to 0.2 eV and 0.1 eV, respectively.
Figure 5.4: Thermalization of a $16 \times 16 \times 16$ simulation cell with the lattice subsystem coupled to a Langevin heat bath at the temperature $T = 800$ K. Subset (a) shows the time evolution of the lattice and the spin temperatures while subset (b) shows the magnetization per atom. The anisotropy coefficients $C_1$ and $C_2$ were set to 0.2 eV and 0.1 eV, respectively.
Figure 5.5: Thermalization of the spin subsystem under varying anisotropy strengths: (a) varying the first order anisotropy coefficient $C_1$ while the second order coefficient $C_2$ set to zero, (b) varying $C_2$ while $C_1$ held constant at 0.2 eV. The lattice subsystem is coupled to a Langevin heat bath at the temperature $T = 800$ K. A 16 × 16 × 16 simulation cell was used.
Figure 5.6: Thermalization of the spin subsystem under varying $C_2$ values with $C_1$ set to zero. The lattice subsystem is coupled to a Langevin heat bath at the temperature $T = 800$ K. A $16 \times 16 \times 16$ simulation cell was used.

Figure 5.7: Thermalization of the spin subsystem under varying vacancy concentrations, with lattice subsystem coupled to a Langevin heat bath at the temperature $T = 800$ K. Anisotropy coefficients $C_1$ and $C_2$ were set to 0.2 eV and 0.1 eV, respectively. A $16 \times 16 \times 16$ simulation cell was used.
Chapter 6

Replica-exchange Wang–Landau study of the magnetic phase transition in bcc iron

6.1 Accuracy and scalability of the parallel framework

To investigate the accuracy and scalability of the parallel replica-exchange Wang–Landau scheme, we first perform simulations on a rigid lattice with atoms frozen at perfect bcc lattice positions. With the rigid lattice constraint, the Hamiltonian (2.35) reduces to simple Heisenberg model with nearest and next-nearest neighbor interactions. The possible energies of the system lie within the range \([-N\epsilon_0, N\epsilon_0]\), where \(\epsilon_0 \approx 0.14\,\text{eV}\) is the absolute value of the ground state energy per spin as given by the exchange interaction (2.52). As our primary interest is the thermodynamic behavior near the critical temperature for the ferromagnetic–paramagnetic transition, we impose minimum and maximum energy cutoffs and sample configurations within a restricted global energy range, \([E_{\text{min}}, E_{\text{max}}]\). This reduction drastically reduces the computational cost of sampling rare configurations at extremely
low and high energies, which potentially becomes a bottleneck in serial Wang–Landau simulations. The reduced energy range is still large enough though that the random walkers are able to visit all contributing microstates; therefore, this reduction does not introduce any systematic errors.

To compare results for the parallel and serial Wang-Landau schemes, we chose a relatively small system size \( L = 10 \) and a global energy range \([-260 \text{ eV}, 120 \text{ eV}]\) that are accessible by the serial method within a fairly reasonable time. For checking the convergence of \( g(E) \), we used the parameter values from the original Wang-Landau paper [88], an 80% flatness criterion and a final modification factor of \( \ln f_{\text{final}} = 1 \times 10^{-8} \).

We decided that eleven windows \( (h = 11) \) and replica exchanges between neighboring windows proposed every 500 MC sweeps are reasonable choices for the lattice size \( L = 10 \). To discretize the energy space, each window was divided into 500 energy bins, which resulted in a total number of 8750 bins for the whole global energy range and a bin size of \( \delta E \approx 0.043 \text{ eV} \). Since replica exchanges can, by construction, only be accepted if both corresponding replica are in the energy overlap region between two windows, small overlaps lead to low acceptance rates whereas an unnecessarily large overlap downgrades the performance. We found that a moderately large overlap of \( o \approx 75\% \) can be a good choice for maintaining a balance between fast convergence and reasonable acceptance rates. With this choice of the overlap, we observed acceptance rates in the range of 52 – 55% for replica exchanges.

With those chosen values of \( h = 11 \) and \( o = 75\% \), we performed parallel simulations for \( L = 10 \) while employing a single walker per window \( (m = 1) \) for simplicity. Fig. 6.1 shows the time series of a single replica as it performs smooth round-trips across the entire energy range (a) and through all the energy windows (b). Similar behavior was observed for all replicas, verifying that the random walkers are not restricted to certain regions of the energy space.
Figure 6.1: Path of a single replica through the entire energy space (a) and energy windows (b) during the first $5 \times 10^5$ MC sweeps. Replica exchanges are attempted every 500 MC sweeps, acceptance rates are in the range of $52 - 55\%$. The replica completes a round-trip approximately every $7 \times 10^4$ MC sweeps.
Fig. 6.2 (a) compares the density of states obtained from both parallel and serial runs. To ensure a fair comparison, the global energy range for the serial runs was discretized with the same number of bins (8750) as for the parallel runs. Data shown by filled circles were obtained from a single parallel simulation, while the solid line represents the average of 10 independent serial runs, with the standard deviation \( \sigma \) shown in the inset. The absolute difference \( \Delta \) between the results from the serial runs and the parallel run is also shown in the inset for comparison. \( \Delta \) is of the same size as \( \sigma \). Thus, the results from the parallel run are clearly within the error bars of the serial runs.

To accommodate the increase in the global energy range for much larger systems, we increased the number of windows accordingly while keeping the energy window size \( (\Delta E \approx 108.57 \text{ eV}) \) and the overlap \( (o = 75\%) \) constant. For example, for \( L = 40 \) with the global energy range \([-16640 \text{ eV}, 7680 \text{ eV}]\), 893 windows were required. While a serial Wang-Landau simulation would take years to estimate the density of states for \( L = 40 \), the parallel scheme achieved this within two days. Fig. 6.2 (b) shows the specific heat \( (C_V/N) \) derived from the estimated density of states for the system sizes \( L = 10 \) and \( L = 40 \). To reduce statistical fluctuations, we have averaged over the results of 6 independent runs for \( L = 10 \), and 11 runs for \( L = 40 \). For comparison, we also show the results obtained from the serial Wang-Landau simulations for \( L = 10 \). The data from the serial and parallel runs are within the mutual error bars.

The success of any parallel scheme depends not only on its accuracy and precision, but also on the scalability, i.e., the ability to effectively utilize an increasing number of processors. Ultimately, by increasing the number of computing cores one hopes to achieve two types of scaling behavior: to speed up the execution while fixing the problem size (strong scaling), or to increase the problem size without increasing execution time (weak scaling). Here, we will demonstrate the weak scaling behavior of our method using the Heisenberg model as a test case. For this analysis, we performed parallel simulations for lattice sizes \( 10 \leq \)
Figure 6.2: (a) Logarithm of the density of states for the lattice size $L = 10$. The solid line represents the average of 10 independent serial runs, filled dots show results from a single parallel run. The inset (note the logarithmic scale) illustrates the accuracy of the parallel method. Solid line in the inset shows the standard deviation $\sigma$ of the serial results while the dots show the absolute numerical difference $\Delta$ between the serial and parallel results. (b) Specific heat curves as functions of temperature for $L = 10$ and $L = 40$. For $L = 10$, the results from the serial runs are shown for comparison.
Figure 6.3: Relative increase in simulation time versus the system size increase. Filled dots are for parallel runs while the open triangles represent serial runs. Simulation time is determined by the time needed to complete the first Wang-Landau iteration. The number of energy windows $h$ were increased with the increasing system size while keeping the size of the windows and the overlap fixed.

$L \leq 50$, (corresponding to spin numbers $2000 \leq N \leq 250000$ respectively), and measured the number of MC trial moves needed to complete the first Wang–Landau iteration. The results of this study are summarized in Fig. 6.3, where we compare the simulation time for serial runs (triangles) with the parallel performance (circles). For the serial runs, simulation time increases dramatically with system size whereas for the parallel runs it remains almost constant.
6.2 Effect of lattice vibrations on the magnetic phase transition

To investigate the influence of lattice vibrations on the thermodynamic properties near the magnetic phase transition, we performed replica-exchange Wang–Landau simulations on the coupled spin-lattice system described by the Hamiltonian (2.35), excluding the kinetic energy term. To explore the sensitivity of the results to the particular choice of EAM potential, we performed simulations using both Dudarev-Derlet (DD) and Finnis-Sinclair (FS) potentials. As for the exchange interaction, the same pairwise function (2.52) was used. The system size was chosen to be $L = 20$. The corresponding global energy ranges were chosen to be $[-67200 \text{ eV}, -63200 \text{ eV}]$ and $[-67200 \text{ eV}, -62080 \text{ eV}]$, respectively, for the DD and FS potentials. For both cases, 189 energy widows with an overlap $\sigma = 75\%$ were used, and a single walker per window ($m = 1$) was employed. To discretize the energy space, each window was divided into 2000 energy bins. Replica exchanges between neighboring widows were proposed every 60 MC sweeps. With these simulation parameters, we observed acceptance rates for the replica exchanges in the range of $49 - 55\%$. For checking the convergence of $g(E)$, an 80% flatness criterion and a final modification factor of $\ln f_{\text{final}} = 1 \times 10^{-8}$ were used. For both potentials, the full convergence of $g(E)$ was achieved in less than a week.

To reduce statistical fluctuations in the estimated thermodynamic quantities, we averaged over the results of 15 independent runs for the DD potential, and 11 runs for the FS potential. Fig. 6.4 shows the comparison of the temperature dependence of the internal energy per atom obtained for the two potentials. For the whole temperature range considered, the internal energy per atom obtained for the FS potential is approximately $0.03 - 0.04 \text{ eV}$ higher than that for the DD potential. Fig. 6.5 shows the specific heat curves for the two potentials, along with the results obtained from the rigid lattice (spin only) simulations for the same system size. Also shown in the subset (a) are the experimental results for the
Figure 6.4: Comparison of the temperature dependence of the internal energy for coupled spin-lattice systems of size \( L = 20 \) using the Dudarev-Derlet ["spin + lattice (DD)"] and Finnis-Sinclair ["spin + lattice (FS)"] potentials.

constant-pressure heat capacity \( C_P \), and the corresponding \( C_V \) values calculated from the \( C_P \) data [124] using the relation \( C_V = C_P - VT\alpha^2/\beta_T \), where \( \alpha \) and \( \beta_T \) are the thermal expansion coefficient and the isothermal compressibility, respectively. Due to the lack of thermal expansion coefficient data, \( C_V \) values above 1000 K are not given [124]. For a fair comparison with the experimental results, we have added \( \frac{3}{2}k_B \) to the DD and FS results to include the contribution of the kinetic energy based on the equipartition theorem. For the rigid lattice results, \( 3k_B \) was added to include the contribution of both the kinetic energy and the lattice potential energy. The vertical arrows in both (a) and (b) mark the Curie temperature \( T_C^{exp} \approx 1043 \) K as predicted by the peak position of the experimental \( C_P \) curve. The peak in the specific heat corresponding to the rigid lattice simulations is approximately 30 K higher than the experimental Curie temperature. The introduction of lattice vibrations
Figure 6.5: Specific heat as a function of temperature for $L = 20$ with [“spin + lattice (DD)” and “spin + lattice (FS)”] and without [“spin only”] the influence of the lattice vibrations; (a) expanded temperature range [500 K, 1200 K] including the experimental results for $C_P$ obtained from Ref. [124] and the corresponding $C_V$ values calculated from the $C_P$ data; (b) a close-up view in the vicinity of the peak positions. The vertical arrows in both (a) and (b) mark the Curie temperature $T_C^{exp} \approx 1043$ K as predicted by the peak position of the experimental $C_P$ curve.
further pushes the peak position to higher temperatures by several degrees. Moreover, lattice vibrations reduces the amplitude of the peak, an effect which is more pronounced for the case of the DD potential.
Chapter 7

Conclusions

In this work, we have investigated the dynamic and thermodynamic behavior of bcc iron using a unified simulation model that treats the atomic coordinates and the orientations of atomic spins as independent variables. Our Hamiltonian consists of a non-magnetic potential that only depends on the atomic positions, and a Heisenberg-like classical spin-dependent interaction. The coupling between the lattice and the spin subsystems is established via a distance-dependent exchange interaction derived from first-principles. As for the non-magnetic potential, we chose two well-established empirical potentials based on the embedded atom formalism: Dudarev-Derlet and Finnis-Sinclair.

From this spin-lattice Hamiltonian, we obtained the three coupled equations of motion which describe the simultaneous dynamics of the translational (i.e. atomic coordinates and velocities) and spin degrees of freedom. These equations lay the foundation for the unified simulation method that we call the “combined molecular and spin dynamics”, or MD-SD. To numerically solve these equations, we employed an algorithm based on the second-order Suzuki-Trotter decomposition of the non-commuting operators, and were able to achieve stable numerical solutions over long time periods (\(\sim 1\) ns) with good energy and magnetization conservation.
To characterize the collective excitations in our system, we have performed microcanonical MD-SD simulations starting from well-equilibrated initial states drawn from the Canonical ensemble at temperatures $T = 300\,\text{K}$ and $T = 800\,\text{K}$. From the trajectories of these simulations, we have calculated the space- and time-displaced correlation functions associated with the atomic and spin variables. The Fourier transforms of these quantities, namely, the dynamic structure factors, directly reveal information regarding the vibrational and magnetic excitation modes. For small $q$ values, the dispersion relations obtained from our simulations at $T = 300\,\text{K}$ agree well with the experimental results, but deviations can be observed for large $q$ values, especially for the magnon dispersion curves. To understand the mutual influence of the phonons and magnons on each other, we have compared our results with that of the stand-alone molecular dynamics and spin dynamics simulations. Due to phonon-magnon coupling, we observe a shift in the characteristic frequencies, as well as a decrease in the lifetimes. These effects become more pronounced as the temperature is increased. The unprecedented resolution provided by our simulations allow us to clearly identify two-spin-wave peaks in the longitudinal spin-spin dynamic structure factor with amplitudes down to six orders of magnitude smaller than that of the highest single spin wave peak observed. In addition to two-spin-wave excitations, in the presence of lattice vibrations, we also observe additional longitudinal magnetic excitations with frequencies which coincide with those of the longitudinal phonons. This is a novel form of excitation that so far has not been detected in inelastic neutron scattering experiments, presumably due to their very low intensities.

We have also introduced a novel extension to the MD-SD formalism for modeling spin-orbit interactions. This approach relies on a valuable but heretofore unexplored concept: The introduction of local magnetic anisotropies due to the symmetry breaking of the local atomic environment. Using canonical MD-SD simulations, we have shown that our improved model facilitates the mutual thermalization of the lattice and the spin subsystems via a ther-
mostat coupled to the lattice subsystem, a task that cannot be achieved with the original formulation. We observe that the relaxation rate of the spin subsystem is enhanced as the target temperature of the lattice thermostat increases. Moreover, the presence of crystallographic defects such as vacancies further intensifies the local anisotropies and noticeably increases the relaxation rate of the spin subsystem. The relaxation times in our simulations (∼ 100 ps) are of the same order of magnitude as the spin-lattice relaxation times of 3d transition metals as observed in experiments [6].

To study the thermal properties of bcc iron, we performed replica-exchange Wang–Landau simulations with/without the influence of the lattice vibrations. We find that the lattice vibrations marginally effect the transition temperature and the amplitude of the peak in the specific heat curve.

All in all, we have shown that by virtue of state-of-the-art numerical schemes and modern high performance computing systems, it is now possible to perform efficient, high-resolution computer simulations that treat the dynamics of translational and spin degrees of freedom on an equal footing. Our results indicate that the interplay between these two types of degrees of freedom has a noticeable impact on the dynamic behavior of magnetic materials, especially at elevated temperatures. With the interaction potentials chosen appropriately, the model and the numerical approach presented in this thesis can be applied to a wide class of magnetic systems in which the spin interactions can be mapped onto classical Hamiltonians. However, the MD-SD approach is a relatively new field with plenty of room for improvements. One such important improvement would be to incorporate Dzyaloshinskii-Moriya interactions [125, 126], that are known to play a significant role in systems with broken inversion symmetry. Although these interactions completely vanish in perfect crystalline symmetry, they may assume non-zero values as the inversion symmetry is broken due to lattice vibrations. This, among many other examples, is an interesting future direction for the continuation of this project.
Bibliography


