Finite-temperature magnetism of ultrathin films and nanoclusters
PhD Thesis

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Chapter 1

Introduction

Magnetic materials continue to play an ever more important role in modern information technology. Their conventional applications in data storage have expanded due to the widespread use of the giant magnetoresistance[1, 2] and exchange bias[3] effects in hard drives and magnetic memory devices. Furthermore, recent developments in the field have concentrated on taking advantage of the spin information in logic circuits, coupled to the charge degree of freedom of electrons in spintronics[4], in the form of spin waves in magnonics[5], or by concentrating on the topological properties as in skyrmionics[6]. They also continue to attract the interest of scientists working in fundamental research; as a few examples, we mention the recently observed spin[7], topological[8] and skyrmion[9] Hall effects, as well as noncollinear magnetic phases such as spin spirals[10] and skyrmion lattices[11].

Similarly to semiconductor-based technologies, the drive for an increased data density has motivated the miniaturization of devices and the decrease in dimensionality of the applied systems. Ultrathin magnetic films with the thickness of a few atoms and the breadth of a few micrometres or hundred nanometres represent a step in this direction, before the system size reaches clusters consisting of several dozen atoms, such as short one-dimensional chains. Although theoretical calculations are already capable of describing the equilibrium properties of such systems observed experimentally at low temperature, the understanding of temperature effects is surprisingly scarce. Since eventually the proposed new devices should operate in room-temperature environments, it is enticing to try and correct this lack of finite-temperature description.

Ultrathin ferromagnetic Fe layers on W(110) represent the first two-dimensional system where the anisotropy of the spin wave spectrum due to the Dzyaloshinsky-Moriya interaction[12, 13] was predicted theoretically[14], and later also demonstrated experimentally using spin-polarized electron energy loss spectroscopy[15, 16]. Although experiments[17] and simulations[18] have indicated that the spin wave frequencies in the system decrease as the temperature is increased, no quantitative theoretical description of this effect has been given.

The Dzyaloshinsky-Moriya interaction may also lead to the formation of a spin spiral state in the system, where the localized magnetic moments are no longer parallel to each other as in the ferromagnetic state. Using spin-polarized scanning tunnelling microscopy, it was demonstrated in [19] that the magnetic ground state of Fe double-layer on W(110) is such a spin spiral state. Furthermore, it was observed[20] that the spiral modulation disappears from the system around 200 K, and is replaced by in-plane ferromagnetic order. Once again, the theoretical background of this reorientation transition has remained
unexplored so far.

In the presence of external magnetic field applied perpendicularly to the surface of the ultrathin film, the spin spiral state created by the Dzyaloshinsky–Moriya interaction may transform into a hexagonal lattice of magnetic skyrmions[21, 22]. This has been first observed experimentally in Fe monolayer on Ir(111) surface with Pd overlayer[23]. The following experimental and theoretical investigations of the system[24–27] focused on the ground state and low-temperature properties of the system. Based on the experimental data available for the bulk system MnSi[28, 29], the destruction of the skyrmion lattice state by thermal fluctuations does not correspond to a simple second-order phase transition, and therefore is also worth investigating in ultrathin films.

The formation of long-range order at finite temperature is prohibited in one-dimensional systems with short-ranged interactions such as the classical Ising model[30]. However, it was experimentally demonstrated in [31] that the magnetization curve of monatomic Co chains located in the step edges of Pt(997) surface shows hysteresis, effectively behaving ferromagnetically at low temperature for sufficiently short timescales and chain lengths. This phenomenon was explained by the high energy barrier separating the two ground states degenerate due to time-reversal invariance. Combining ab initio calculations with atomistic simulations enables the determination of the height of such energy barriers.

In this thesis, we will use electronic structure calculations based on density functional theory to describe realistic ultrathin films and nanoclusters. The focus of the ab initio calculations is the construction of a model system, where the spin degree of freedom is represented by a classical unit vector. After this has been performed, we will investigate the finite-temperature properties of such classical systems by applying theoretical methods developed for three-dimensional materials and noninteracting magnetic particles. The temperature effects will only be taken into account in the classical model, not in the ab initio determination of the electronic structure. We will compare the theoretical predictions to atomistic spin dynamics and Metropolis Monte Carlo simulations, and discuss the limits of applicability of both the theoretical and the simulational description.

Chapters 2–7 discuss the theoretical background of this work. The electronic structure of the systems will be determined by applying the screened Korringa–Kohn–Rostoker method[32–34] based on density functional theory in chapter 2, culminating in the construction of a classical spin model defined on the atomic level. The excitations of this classical system called spin waves represent the focus of chapter 3. In chapter 4, we will present two finite-temperature theoretical methods, one of which is based on spin waves, while the other is a mean-field theory. In chapter 5, we will discuss how temperature effects can be included in the equation of motion of the spins, by presenting the stochastic Landau–Lifshitz–Gilbert equation[35–38]. We will also discuss and construct appropriate numerical solvers for the equation, which will be used during the spin dynamics simulations. The focus of chapter 6 will be the noncollinear spin spiral and skyrmion lattice phases; we will introduce the appropriate terminology, and discuss the characteristics of the ground states and the spin wave excitations. Finally, in chapter 7 we will summarize the inputs and outputs of the numerical simulation methods.

The results of the thesis will be presented in chapters 8–12, each containing an overview of the previous experimental and theoretical studies performed on the system in question. Chapter 8 will concern the spin wave spectrum of a ferromagnetic monolayer representing Fe on W(110), and how the spin wave frequencies may be determined from simulations and theory. In chapter 9, we will discuss the temperature-dependent spin reorientation
transition in Fe double-layer on W(110), and its possible explanation within mean-field
theory. The topic of chapter 10 is the different spin spiral ground states obtained from
\textit{ab initio} calculations in an Fe monolayer on Ta(110), and the phase transitions occurring
between these states depending on the geometry of the substrate and as a consequence
of thermal excitations. In chapter 11, we will discuss how the strong fluctuations at
higher temperature cause a finite skyrmion lifetime in PdFe bilayer on Ir(111) surface.
Finally, in chapter 12 we will test the applicability of the numerical integration methods
from chapter 5, and use a chain of ten Co atoms on Au(001) surface as an example for
discussing thermal equilibrium properties and switching times.
Chapter 2

Multiple scattering theory

The time-independent properties of a quantum many-body system may be determined by solving the stationary Schrödinger equation; that is, finding the eigenvalues $E_n$ and the eigenvectors $\Psi_n$ of the Hamiltonian $H$ that satisfy

\[(E_n - H) \Psi_n = 0. \tag{2.1}\]

In coordinate representation, one faces two difficulties when determining the wave functions $\Psi_n$: firstly, they will depend on the position of all $N$ atoms considered, $N \sim 10^{23}$ in solids; secondly, these positions may take values in a volume which is large compared to the atomic scale on which the wave function shows oscillating behaviour. Therefore, the accurate numerical solution of (2.1) would require incredible computational capacities. Instead of the direct solution, one has to rely on different approximations.

Regarding the first problem, the interacting many-particle system is usually replaced by a single-particle system with some effective interaction. This simplification will be discussed within the terms of relativistic density functional theory. The second problem may be simplified by solving equation (2.1) for an atomic-scale volume and expanding it to the whole space by taking into account scattering events between the atomic cells. For this purpose we will apply the Körringa–Kohn–Rostoker multiple scattering theory[32][33]. Since the cells and scattering events are handled in real space instead of momentum space, the method is well-suited for describing systems which lack translational invariance in three dimensions. In particular, it will be used in this thesis to describe the magnetic interactions in two-dimensional surfaces and clusters containing only a few atoms.

In this chapter we will only introduce the definitions of the basic quantities; a somewhat more thorough description is given in appendix A. Readers more interested in the details are referred to a textbook on density functional theory[39] or a review on Köringga–Kohn–Rostoker theory[40, 41].

2.1 Density functional theory

Instead of solving (2.1), we will find the eigenvalues and eigenvectors of the single-particle Kohn–Sham–Dirac equation

\[ (e\alpha \mathbf{p} + \beta mc^2 + V_s + \muB\beta \mathbf{S}_B) \psi_n = \varepsilon_n \psi_n, \tag{2.2} \]
with $\mu_B = \frac{e}{2m}$ the Bohr magneton, $c, \hbar, e$ and $m$ the speed of light, the Planck constant, the charge and mass of the electron, respectively. The matrices $\alpha, \beta$ are defined as

\[
\alpha^i = \gamma^0 \gamma^i, \\
\beta = \gamma^0,
\]

where the $\gamma^\mu, \mu = 0, 1, 2, 3$ matrices form a representation of the Grassmann algebra

\[
\{ \gamma^\mu, \gamma^\nu \} = 2\eta^{\mu\nu} I,
\]

with $\eta^{\mu\nu}$ the Minkowski metric tensor. The matrix $\Sigma$ in the Dirac representation reads

\[
\Sigma = \begin{bmatrix} \sigma & 0 \\ 0 & -\sigma \end{bmatrix},
\]

with $\sigma$ the vector formed from the Pauli matrices.

The Kohn–Sham theorem\cite{42} states that for every interacting electronic system with potential $V_0$ there exists a single-particle equation with an effective potential $V_s$ which has the same electron density in the ground state. The connection between the two potentials is given by

\[
V_s (r) = V_0 (r) + \int \frac{k C e^2}{|r - r'|} n_0 (r') \, d^3 r' + V_{xc} (r) = V_0 (r) + V_{\text{Hartree}} (r) + V_{xc} (r),
\]

with an analogous expression between the real $B$ and effective single-particle $B_s$ magnetic fields,

\[
B_s (r) = B (r) + B_{xc} (r).
\]

The exchange-correlation potential $V_{xc} (r)$ and magnetic field $B_{xc} (r)$ contain the effects of the interactions between the electrons in the original system. Unfortunately, their explicit form is not known; we will use the local spin density approximation, where at every point in space $r$ they are expressed by the local electron density

\[
n (r) = \sum_n \psi_n^\dagger (r) \psi_n (r)
\]

and magnetization

\[
m (r) = -\mu_B \sum_n \psi_n^\dagger (r) \beta \Sigma \psi_n (r).
\]

Since (2.2) is a Dirac equation, it also includes relativistic effects such as the spin–orbit interaction. These are especially strong in elements with many electrons such as 5d metals, and are essential for determining the magnetic interactions in the systems discussed in this thesis.

### 2.2 Korringa–Kohn–Rostoker theory

In the noninteracting system described by (2.2), we can calculate the expectation value of single-particle operators $A$ as

\[
\langle A \rangle = \sum_n f (\varepsilon_n) \langle \psi_n | A | \psi_n \rangle,
\]

(2.11)
where \( f(\varepsilon_n) = \left(e^{\beta(\varepsilon_n - \mu)} + 1\right)^{-1} \) is the Fermi distribution. Examples include the electron density \( n(\mathbf{r}) \) (2.9) and magnetization \( \mathbf{m}(\mathbf{r}) \) (2.10).

In scattering theory, one introduces the single-particle Green function

\[
(z - H(\mathbf{r})) G(z; \mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}'),
\]

(2.12)
defined for complex \( z \) values for which the Dirac equation (2.2) has no solution. The expectation values (2.11) may also be expressed as

\[
\langle A \rangle = -\frac{1}{\pi} \int_{-\infty}^{\infty} \int f(\varepsilon) \text{ImTr} \left( A(\mathbf{r}) G^+(\varepsilon; \mathbf{r}, \mathbf{r}') \right) d^3\mathbf{r} d\varepsilon,
\]

(2.13)
where \( G^+ \) denotes the limit of the Green function as \( z \) approaches the real axis \( \varepsilon \) from the direction of positive imaginary part. At zero temperature, the integration contour can be deformed to any contour in the upper complex semiplane starting at \( -\infty \) (or in practice, a sufficiently low energy value) and ending at \( \varepsilon_{\text{Fermi}} \), since the Green function is regular here, while it is singular for the spectrum of \( H \) along the real axis. On such a contour, the numerical evaluation of the integral with a desired accuracy generally requires significantly less points than along the real axis. For most applications, 12-16 energy points along a semicircle contour are sufficient.

In the Korringa–Kohn–Rostoker method, the space is divided into atomic cells, and the potential \( V \) is similarly divided as

\[
V = \sum_{\text{cells } i} V_i,
\]

(2.14)
where \( V_i \) is only finite within a single cell \( i \). One of the usual algorithms of dividing the space is called the muffin-tin method[43], where the system consists of nonoverlapping spheres and an interstitial region of constant potential. Here we will use the atomic sphere approximation, where the solid is divided into Voronoi polyhedra around centres of the atoms, and these polyhedra are replaced by spheres of the Wigner–Seitz radius. In this case, the total volume of the atomic spheres is equal to the system volume, but the spheres will slightly overlap.

If the cells and the atomic potentials have spherical symmetry, it is advisable to use effective potentials in the Kohn–Sham equation (2.2) which reflect this symmetry, that is,

\[
V_{xc,i}(\mathbf{r}) = V_{xc,i}(r),
\]

(2.15)
\[
B_{xc,i}(\mathbf{r}) = B_{xc,i}(r) \mathbf{e}_i,
\]

(2.16)

In this case, (2.2) simplifies to a radial equation, which has to be solved within a single cell. Although we will take advantage of this simplification, we note that there exist so-called full-potential methods[44], where the potential or the unit cells do not have spherical symmetry.

The information about the potential and the solutions of the Kohn–Sham–Dirac equation at a single site is encoded in the \( t \) matrix

\[
t(\varepsilon) = \left\{ t^{QQ'}(\varepsilon) \delta_{ij} \right\},
\]

(2.17)
where \( Q, Q' \) denote total angular momentum quantum numbers, appropriate for describing spherically symmetric systems. The propagation between the cells is described by the
matrix representation of the free Green function, called the free structure constant, and expressed as

\[ G_0 (\varepsilon) = \left\{ G_{0,ij}^{QQ'} (\varepsilon) (1 - \delta_{ij}) \right\}. \]  \hfill (2.18)

The full system containing all the atomic cells is characterized by the matrix of the so-called scattering path operator \( \tau \), defined as

\[ \tau (\varepsilon) = \left\{ \tau_{ij}^{QQ'} \right\}, \]  \hfill (2.19)

which can be calculated from the known quantities \( t \) and \( G_0 \) as

\[ \tau (\varepsilon) = (t^{-1} (\varepsilon) - G_0 (\varepsilon))^{-1}. \]  \hfill (2.20)

Finally, one has to express the Green function (2.12) with the scattering path operator

\[ G(\varepsilon; r_i + R_i, r_j' + R_j) = \frac{\varepsilon + mc^2}{2mc^2} \sum_{Q,Q'} Z_i^Q (\varepsilon; r_i) \tau_{ij}^{QQ'} (\varepsilon) Z_j^{Q'} (\varepsilon; r_j') \]

\[ - \delta_{ij} \frac{\varepsilon + mc^2}{2mc^2} \sum_Q \left( Z_i^Q (\varepsilon; r_i) J^Q (\varepsilon; r_j') \Theta (r_j' - r_i) \right. \]

\[ + \left. J^Q (\varepsilon; r_i) Z_i^Q (\varepsilon; r_j') \Theta (r_i - r_j') \right), \]  \hfill (2.21)

where \( R_i \) denotes the position vector of the centre of cell \( i \) in the global coordinate system, \( Z_i^Q \) and \( J^Q \) are solutions of (2.2) at site \( i \) and for free electrons, while \( \Theta (x) \) is the Heaviside step function. For a more thorough discussion of the theory see appendix A.8.

### 2.3 The scattering path operator for surfaces and clusters

Equation (2.20) provides a way of calculating the scattering path operator in real space, which can be used to determine expectation values of single-particle operators by using (2.13) and (2.21). Theoretically, the \( t, G_0 \) and \( \tau \) matrices are infinite in both the site \( i \) and angular momentum \( Q \) indices. The angular momentum expansion is usually truncated by choosing a maximum value \( l_{\text{max}} \) for the orbital angular momentum quantum number. Due to spin and magnetic quantum numbers, this will lead to \( 2 (l_{\text{max}} + 1)^2 \) values of the \( Q \) index. Choosing \( l_{\text{max}} = 2 \) or \( l_{\text{max}} = 3 \) usually provides a satisfactory description of the \( d \)-electron metallic systems considered in this thesis.

The real space site indices \( i \) cannot be truncated in a similar way. For bulk calculations, meaning systems with discrete translational invariance in three dimensions, it is straightforward to solve equation (2.20) in Fourier space,

\[ \tau_k (\varepsilon) = (t^{-1} (\varepsilon) - G_{0,k} (\varepsilon))^{-1}. \]  \hfill (2.22)

Here the \( t \) matrix is the same for every lattice point, and all matrix sizes in (2.22) are determined by \( l_{\text{max}} \). The real-space matrices may be calculated by inverse Fourier transformation; numerically, their accuracy will depend on how many \( k \) points in the Brillouin zone \( \tau_k (\varepsilon) \) was determined for.
Figure 2.1: Sketch of the different concepts discussed in section 2.3. Surfaces consisting of layers are calculated within the screening framework, while the embedding method is used for clusters built up from several atoms.

The ultrathin films considered in this thesis only have discrete translational invariance in two dimensions, and Fourier transformation can only be performed in the plane. This step simplifies (2.20) to a one-dimensional problem.

Within the so-called screened Korringa-Kohn-Rostoker method[34], the Green function matrix is first determined for a system formed by constant repulsive potentials,

\[ G_r (\varepsilon) = G_0 (\varepsilon) (I - t_r (\varepsilon) G_0 (\varepsilon))^{-1}, \]

(2.23)

where the r index denotes that this will be the reference system for further calculations. Due to the high potential barriers, the wave functions and correspondingly the Green function will decay exponentially in space for energy values \( \varepsilon \) near the Fermi level of the metal, so they can be neglected between layers sufficiently far away. In practice, the screening is implemented by dividing the system into so-called principal layers, each consisting of 3-4 atomic layers, and \( G_r \) is only taken to be finite inside the principal layers and between neighbouring principal layers.

The reference system can be considered translationally invariant in three dimensions. If we consider an ultrathin film consisting of a few principal layers between the semi-infinite bulk and the semi-infinite vacuum, the \( t \) matrix can be written as a sum of a reference and a screened matrix,

\[ t (\varepsilon) = t_r (\varepsilon) + \Delta t_n (\varepsilon). \]

(2.24)

The size of the screened \( \tau \) matrix \( \tau_s \) is determined by the number of principal layers besides \( l_\text{max} \). Although the matrix equation (2.20) is still infinite in one dimension, it is possible to express \( \tau_s \) analytically if \( G_r \) is tridiagonal in the principal layer blocks[34]. The actual \( \tau \) matrix of the system may finally be determined by the site-diagonal transformation

\[ \tau = t [\Delta t_n]^{-1} \tau_s [\Delta t_n]^{-1} t - t [\Delta t_n]^{-1} t + t. \]

(2.25)
For the description of clusters of atoms, the embedding technique [45] is a more suitable choice. Firstly, the $t$ and $\tau$ matrices have to be determined for a reference system which does not contain the embedded cluster. After obtaining the $t_\epsilon$ and $\tau_\epsilon$ matrices, we define the embedded $t$ matrix as the difference between the real system and the reference one,

$$[\Delta t_\epsilon]^{-1} = t^{-1}_\epsilon - t^{-1}.$$  \hspace{1cm} (2.26)

Note that contrary to (2.24), here the difference is defined in terms of the inverse $t$ matrices. The $\tau$ matrix of the system may be calculated as

$$\tau = \tau_\epsilon (I - [\Delta t_\epsilon]^{-1} \tau_\epsilon)^{-1}. \hspace{1cm} (2.27)$$

Since $[\Delta t_\epsilon]^{-1}$ only differs from zero for the atoms in the cluster, it can be proven that the $\tau$ matrix restricted to the cluster $\tau_c$ may be calculated as

$$\tau_c = \tau_{\epsilon,c} (I - [\Delta t_\epsilon]^{-1} \tau_{\epsilon,c})^{-1}. \hspace{1cm} (2.28)$$

For a cluster containing $N$ atoms, the matrices in equation (2.28) are of linear size $2N (l_{\text{max}} + 1)^2$.

2.4 Expectation values of single-particle operators

After calculating the $\tau$ matrix and the Green function from (2.21), equation (2.13) defines the expectation values of single-particle operators. The electronic density at point $r$ and energy $\epsilon$ is given by

$$n(r, \epsilon) = -\frac{1}{\pi} f(\epsilon) \text{Im} \text{Tr} G^+(\epsilon; r, r). \hspace{1cm} (2.29)$$

When integrated over the variable $\epsilon$, this leads to the density at point $r$,

$$n(r) = -\frac{1}{\pi} \int_{-\infty}^{\infty} f(\epsilon) \text{Im} \text{Tr} G^+(\epsilon; r, r) \, d\epsilon, \hspace{1cm} (2.30)$$

which must be substituted back into the potentials $V_{cc}(r)$ and $B_{cc}(r)$ appearing in the Kohn–Sham–Dirac equation (2.2). Performing the integration in real space instead of energy yields the density of states $n(\epsilon)$.

In this thesis, the magnetism of the system will be characterized by the localized spin and orbital magnetic moments in a given cell. The expectation value of the spin operator at site $i$ is given by

$$S_i = -\frac{1}{\pi} \int_{-\infty}^{\infty} \int_{\text{cell } i} f(\epsilon) \text{Im} \text{Tr} (\beta \Sigma G^+(\epsilon; r, r)) \, d^3r \, d\epsilon, \hspace{1cm} (2.31)$$

while the spin magnetic moment is calculated as $M_i^{\text{spin}} = g \mu_B S_i$ with the gyromagnetic factor $g = 2$.

The total angular momentum at site $i$ is defined as

$$J_i = -\frac{1}{\pi} \int_{-\infty}^{\infty} \int_{\text{cell } i} f(\epsilon) \text{Im} \text{Tr} (J G^+(\epsilon; r, r)) \, d^3r \, d\epsilon, \hspace{1cm} (2.32)$$

14
where $J$ is the matrix of the total angular momentum operator in spinor and $Q$ indices. The orbital magnetic moment at cell $i$ can be calculated as $M_i^{\text{orbital}} = \mu_B (J_i - S_i)$. The knowledge of the magnetic moments is necessary in the self-consistent calculations because in the ground state, the magnetic moment at site $i$ must be parallel to the direction of the exchange-correlation field $B_{xc,i}$, denoted by $e_i$ in (2.16). Therefore, the calculated magnetic moments determine $e_i$ in the next iteration step, just as the electronic density determines the radial part of the potential.

2.5 Effective torque acting on the spins

As discussed in section 2.4, the self-consistent calculation of the ground state requires the rotation of the direction of the exchange-correlation field $e_i$ between the iteration steps. However, it is also possible to determine the ground state of a system with the constraint that the magnetization directions are fixed during the calculation[46]. This makes it possible to determine an energy expression as a function of the directions of the localized magnetic moments. This is the basic idea behind mapping the system onto a model which only takes into account the magnetic moment directions as degrees of freedom. This mapping is justified by the adiabatic decoupling[47] of the longitudinal and transversal spin fluctuations at a given site. The length of the spin on a given site can change as a consequence of the motion of electrons between the atoms, or due to the excitement between different orbitals on a single atom. The relevant electronic energy scales, such as the bandwidth or the on-site energy in the Hubbard model, fall in the eV range. On the other hand, the rotational motion of the spins is governed by interatomic Heisenberg exchange coefficients between the spins, on the order of approximately 10 meV. This way, it is possible to identify localized magnetic moments in the system which are fixed to atomic cells and their direction only varies between the cells, the dynamics of these moments may be described by dynamical equations which only treat the significantly faster electronic fluctuations as averaged quantities. The presence of localized magnetic moments was confirmed experimentally not only in insulators, but also in most strong itinerant systems such as the metallic ferromagnets Fe, Co and Ni[48].

Instead of fixing the magnetization direction, we will consider rotations of the directions $e_i$ of the exchange-correlation field around the vector $e_{ri}$ by angle $\beta_{ri}$, and calculate the modification of the energy of the system. Instead of the total energy discussed in appendix A.4, we will consider the band energy

$$E_{\text{band}} = \sum_n \epsilon_n - \epsilon_{\text{Fermi}} N = - \int_{-\infty}^{\epsilon_{\text{Fermi}}} N(\epsilon) \, d\epsilon,$$

where $N(\epsilon) = \int_{-\infty}^{\epsilon} n(\epsilon') \, d\epsilon'$ is the integrated density of states. Although the band energy does not take into account that the original electron system is interacting, the force theorem[49] states that its lowest-order correction $\Delta E_{\text{band}}$ for infinitesimal modifications of the potential around the ground state coincides with that of the total energy. The advantage of using the band energy is that the correction to the integrated density of states $\Delta N(\epsilon)$ can be calculated exactly within scattering theory using the Lloyd formula[50].

If the rotation of $e_i$ is performed at a single site $i$, this formula yields

$$\frac{\partial E_{\text{band}}}{\partial \beta_{ri}} = \frac{1}{\pi} \int_{-\infty}^{\epsilon_{\text{Fermi}}} \text{ImTr} \left( \frac{i}{\hbar} [e_{ri} J_i t_i^{-1}] \tau_{ii} \right) d\epsilon,$$

(2.34)
Figure 2.2: Direction $e_i$ of the exchange-correlation field at site $i$. The rotation around the orthogonal vectors $e_{1i}, e_{2i}$ by angles $\beta_{1i}, \beta_{2i}$ will lead to a change in the band energy $E_{\text{band}}$ as described by (2.34) and (2.35).

which is the exact derivative of the band energy with respect to an infinitesimal rotation angle.

If the direction of the exchange-correlation field is rotated at two sites $i$ and $j$, the second derivative of the band energy with respect to the angle variables $\beta_{ri}, \beta_{pj}$ can be calculated similarly as\[51\]

$$
\frac{\partial^2 E_{\text{band}}}{\partial \beta_{ri} \partial \beta_{pj}} = \frac{1}{\pi} \int_{-\infty}^{2\pi_{\text{norm}}} \text{Im} \frac{1}{\hbar^2} \text{Tr} \left( \left[ e_{ri} J, t_i^{-1} \right] \tau_{ij} \left[ e_{pj} J, t_j^{-1} \right] \tau_{ji} \right. \\
- \left. \delta_{ij} \frac{1}{2} \left\{ [e_{ri} J, [e_{pi} J, t_i^{-1}]] + [e_{pi} J, [e_{ri} J, t_i^{-1}]] \right\} \tau_{ji} \right) \, d\varepsilon. \tag{2.35}
$$

The first and second derivatives need not be calculated for arbitrary rotation axes $e_{ri}$, since every infinitesimal rotation of the direction $e_i$ may be expressed as a linear combination of rotations around two vectors ($r = 1, 2$), which are linearly independent from each other and $e_i$. We will choose these fixed directions in such a way that the vectors $e_{1i}, e_{2i}, e_i$ form an orthonormal right-handed system as shown in figure 2.2. The rotation angles $\beta_{1i}, \beta_{2i}$ are defined to be positive for right-handed rotations.

Equations (2.34)-(2.35) prescribe a way of minimizing the band energy of the system by expressing an effective torque acting on the directions of the exchange-correlation field at different lattice sites. These torques can be used to calculate the noncollinear ground state of a magnetic system self-consistently\[52\]. In the ground state, the direction of the magnetic moments (2.31) will coincide with the directions of the exchange-correlation fields. We shall suppose that the direction of the magnetic moments will stay close to that of the exchange-correlation field even if the system is not in the ground state.
Therefore, equations (2.34)-(2.35) may be interpreted as torques acting on the direction of the magnetic moment. This will offer an opportunity for simulating the dynamics of the system, either by using expressions (2.34)-(2.35) directly or mapping the system onto a model Hamiltonian which only contains the spin degrees of freedom.

2.6 Mapping to a model Hamiltonian

Consider a spin Hamiltonian of the form

\[ H = \frac{1}{2} \sum_{ij} J_{ij}^{\alpha\beta} S_i^\alpha S_j^\beta + \sum_i K_i^{\alpha\beta} S_i^\alpha S_i^\beta. \]  

(2.36)

Here the $S_i^\alpha$ variables are classical unit vectors, $\alpha$ and $\beta$ are Cartesian indices, while $i$ and $j$ denote different sites as before. The interaction between the spins is captured in the coupling tensors $J_{ij}^{\alpha\beta}$ and the on-site anisotropy tensors $K_i^{\alpha\beta}$. It is easy to see that only the symmetric part of $K_i^{\alpha\beta}$ contributes to the energy, and therefore it can be supposed that $K_i^{\alpha\beta}$ is symmetric. Since the spins are normalised, adding a multiple of the identity tensor to $K_i^{\alpha\beta}$ only shifts the energy by a constant value. This means that there is a free parameter in the diagonal of $K_i^{\alpha\beta}$; we will either require $K_i^{\alpha\beta}$ to be traceless or set $K_i^{zz} = 0$. Similarly, we can assume $J_{ij}^{\alpha\beta} = J_{ji}^{\alpha\beta}$, since only this part of the coupling tensor contributes to the energy. The Hamiltonian (2.36) only contains quadratic terms in the spin variables: the odd terms must disappear due to time-reversal invariance, which is a symmetry of the system in the absence of external magnetic field; the higher-order even terms are generally smaller in magnitude than the quadratic terms, and will be omitted from further discussions.

The form of (2.36) imposes no further symmetry requirements in and of itself. For example, the coupling tensor needs not be symmetric; its antisymmetric part

\[ D_{ij}^\gamma = \frac{1}{2} \varepsilon^{\alpha\beta\gamma} J_{ij}^{\alpha\beta} \]  

(2.37)

is called the Dzyaloshinsky–Moriya vector. This type of exchange interaction was discovered by Dzyaloshinsky[12] and by Moriya[13]; it appears as a consequence of the relativistic spin-orbit coupling. The Dzyaloshinsky–Moriya interaction term in the Hamiltonian (2.36) may be rewritten as

\[ E_{DM} = D_{ij} (S_i \times S_j) \]  

(2.38)

in vector notation.

Similarly to the Dzyaloshinsky–Moriya interaction, the on-site anisotropy term only appears in relativistic calculations. On the other hand, the isotropic part of the tensor,

\[ J_{ij} = \frac{1}{3} J_{ij}^{\alpha\alpha}, \]  

(2.39)

can also be obtained within nonrelativistic theories including the spin. The corresponding energy expression in (2.36) reads

\[ E_{iso} = J_{ij} S_i S_j \]  

(2.40)

in vector notation, describing the well-known classical Heisenberg model with scalar coupling coefficients.
The symmetric, traceless part of $J_{ij}^{\alpha\beta}$ also appears due to relativistic effects in our calculations. We mention that the classical dipolar interaction between spins $S_i$ and $S_j$ at relative position $R_{ij}$,

$$E_{\text{dipolar}} = \frac{\mu_0}{4\pi} M_i M_j \left( \frac{S_i S_j}{R_{ij}^5} - 3 \frac{(S_i R_{ij}) (S_j R_{ij})}{R_{ij}^7} \right),$$

is also described by a symmetric, traceless interaction tensor. The dipolar interaction must be added manually to the $J_{ij}^{\alpha\beta}$ tensors calculated from \textit{ab initio} methods; however, in most calculations we omit this contribution as it is significantly weaker than the relativistic effects for nanometre-sized samples.

The symmetry of the considered system may impose further conditions on the coupling and anisotropy tensors. For example, the discrete translational invariance of a lattice dictates

$$J_{ij}^{\alpha\beta} = J^{\alpha\beta} (R_i - R_j),$$

and that $K_i^{\alpha\beta}$ must be the same for all translationally equivalent atoms; in this case the $i$ index only differentiates between atoms in different layers in a thin film or sublattices. The point group symmetries lead to additional requirements; for example, the Dzyaloshinsky–Moriya vector must disappear in systems with inversion symmetry\cite{53}. However, in this thesis we will only consider ultrathin films and clusters where the inversion symmetry is absent.

If we identify the direction of the exchange-correlation field $e_i$ in section 2.5 with the classical unit vectors $S_i$ representing the spin magnetic moments, derivatives of the form (2.34)-(2.35) may also be calculated from the model Hamiltonian (2.36). Using the notations of figure 2.2 with $S_i = e_i$, the first and second derivatives of (2.36) with respect to the angle variables $\beta_{1i}, \beta_{2i}$ read

$$\frac{\partial H}{\partial \beta_{2i}} = \sum_j J_{ij}^{\alpha\beta} e_i^{\alpha} e_j^{\beta} + K_i^{\alpha\beta} \left( e_i^{\alpha} S_j^{\beta} + S_i^{\alpha} e_j^{\beta} \right),$$

$$\frac{\partial H}{\partial \beta_{1i}} = - \sum_j J_{ij}^{\alpha\beta} e_i^{\alpha} S_j^{\beta} - K_i^{\alpha\beta} \left( e_i^{\alpha} S_i^{\beta} + S_i^{\alpha} e_i^{\beta} \right),$$

and

$$\frac{\partial^2 H}{\partial \beta_{2j} \partial \beta_{2i}} = J_{ij}^{\alpha\beta} e_i^{\alpha} e_j^{\beta} \quad \text{for } j \neq i,$$

$$\frac{\partial^2 H}{\partial \beta_{2j} \partial \beta_{1i}} = - J_{ij}^{\alpha\beta} e_2^{\alpha} e_1^{\beta} \quad \text{for } j \neq i,$$

$$\frac{\partial^2 H}{\partial \beta_{1j} \partial \beta_{2i}} = - J_{ij}^{\alpha\beta} e_1^{\alpha} e_2^{\beta} \quad \text{for } j \neq i,$$

$$\frac{\partial^2 H}{\partial \beta_{1j} \partial \beta_{1i}} = J_{ij}^{\alpha\beta} e_2^{\alpha} e_2^{\beta} \quad \text{for } j \neq i,$$
\[
\frac{\partial^2 H}{\partial \beta_{2i}^2} = - \sum_j J_{ij}^{\alpha\beta} S_i^\alpha S_j^\beta - 2K_i^{\alpha\beta} S_i^\alpha S_i^\beta + 2K_i^{\alpha\beta} \epsilon_i^{\alpha\beta} \epsilon_{1i}, \quad (2.49)
\]

\[
\frac{\partial^2 H}{\partial \beta_{1i}^2} = - \sum_j J_{ij}^{\alpha\beta} S_i^\alpha S_j^\beta - 2K_i^{\alpha\beta} S_i^\alpha S_i^\beta + 2K_i^{\alpha\beta} \epsilon_i^{\alpha\beta} \epsilon_{2i}, \quad (2.50)
\]

\[
\frac{\partial^2 H}{\partial \beta_{1i} \partial \beta_{2i}} = - K_i^{\alpha\beta} \left( \epsilon_i^{\alpha\beta} \epsilon_{2i} + \epsilon_i^{\alpha\beta} \epsilon_{1i} \right). \quad (2.51)
\]

The coupling parameters in the Hamiltonian (2.36) are calculated by comparing the values of the second derivatives obtained using the magnetic force theorem in (2.35) to the same derivatives of the model Hamiltonian (2.45)-(2.51). For the nonrelativistic case with scalar couplings this was first done in [54], which was later generalized to relativistic systems in [51]. Since equations (2.45)-(2.51) contain a linear combination of the \( J_{ij}^{\alpha\beta} \) and \( K_i^{\alpha\beta} \) values, one has to solve a linear system of equations; this is described in detail in appendix A.9. We note that there are other ways of finding a correspondence between the \textit{ab initio} energy expression and the model Hamiltonian, such as the spin cluster expansion described in [55]. In this method, the band energy is calculated in the paramagnetic state, where the spin directions have a uniform distribution on the unit sphere.

The accuracy of the determined exchange coefficients depends on the calculation of the second derivatives (2.35). For layered systems, the \( \tau \) matrices are determined in Fourier space as discussed in section 2.3, but the interactions are given in real space. The value of the coupling coefficients may strongly depend on the number of \( k \) points in the Brillouin zone integration, particularly close to the Fermi energy. The on-site anisotropy tensor may be especially susceptible to the numerical details of the calculations, since it is generally one or two magnitudes smaller than the scalar Heisenberg exchange between the nearest neighbours, and it has to be calculated as a difference of two relatively large values, equations (2.49)-(2.50). Changing the geometry and therefore the potential of the system may also have important effects on the coupling constants; this is illustrated in sections 9.1 and 10.1 for specific systems.
Chapter 3

Equation of motion and spin waves

In this chapter we will discuss the dynamics of a nondissipative spin system. The Hamiltonian used here is similar to (2.36) determined during the ab initio calculations, but we also allow for the presence of an external magnetic field by introducing the Zeeman term. This leads to

\[ H = \frac{1}{2} \sum_{ij} J_{ij}^\alpha S_i^\alpha S_j^\alpha + \sum_i K_i^\alpha S_i^\alpha S_i^\alpha - \sum_i M_i B^\alpha S_i^\alpha, \]

(3.1)

with \( M_i \) the magnetic moment at site \( i \), which we will identify with the spin moment calculated from (2.31), since the orbital component is generally small in the discussed systems. This also means that the gyromagnetic factor \( g \) is identified with the spin gyromagnetic factor, and is thus independent of the considered system. The \( S_i \) vectors are parallel to the spin magnetic moment, which points in the opposite direction as the spin angular momentum due to the negative charge of the electrons. Keeping the above considerations in mind, we will simply refer to the \( S_i \) quantities as spin vectors in the following, just as it was done in chapter 2.

Given the Hamiltonian (3.1), one can determine the ground state and the dynamics of the system. Of the dynamical behaviour, this chapter will only consider the low-energy excitations of the system called spin waves. These can be obtained from the equations of motion of the nondissipative system; the inclusion of damping and finite-temperature effects in the equation of motion will be discussed in chapter 5.

3.1 Quantum ferromagnet

Firstly, we will calculate the equation of motion and the excitations of a quantum ferromagnetic system, then generalize the results to classical systems with more complicated ground states. For this purpose, we will use the simplified Hamiltonian

\[ H = \frac{1}{2} \sum_{ij} J_{ij} \hat{S}_i \hat{S}_j + g \mu_B \sum_i B_i \hat{S}_i, \]

(3.2)

with \( J_{ij} < 0 \) ferromagnetic Heisenberg coupling. We will suppose that all the atoms in the system are equivalent, with spin quantum number \( S \); and that the system has translational invariance, \( J_{ij} = J (\mathbf{R}_i - \mathbf{R}_j) \). The \( \hat{S}_i \) operators in (3.2) satisfy the commutation relations

\[ [\hat{S}_i^\alpha, \hat{S}_j^\beta] = i\delta_{ij} \varepsilon^{\alpha\beta\gamma} \hat{S}_i^\gamma, \]

(3.3)
that is, they correspond to spin angular momentum operators instead of unit vectors parallel to the spin magnetic moment.

The general equation of motion of operator $A$ reads

$$\partial_t A = -\frac{i}{\hbar} [A, H], \quad \text{(3.4)}$$

which for a spin system described by (3.2) simplifies to

$$\partial_t \hat{S}^\alpha_i = -\frac{i}{\hbar} \left[ \hat{S}^\alpha_i, \hat{S}^\beta_j \right] \frac{\partial H}{\partial \hat{S}^\beta_i} = \frac{1}{\hbar} \varepsilon^\alpha\beta\gamma \hat{S}^\gamma_i \frac{\partial H}{\partial \hat{S}^\beta_i}. \quad \text{(3.5)}$$

We shall introduce the effective magnetic field acting on the spins,

$$B_{\text{eff}}^i = -\frac{1}{g\mu_B} \frac{\partial H}{\partial \hat{S}^i}, \quad \text{(3.6)}$$

leading to

$$\partial_t \hat{S}_i = -\gamma \hat{S}_i \times B_{\text{eff}}^i, \quad \text{(3.7)}$$

with $\gamma = \frac{2\mu_B}{\hbar} = \frac{e}{2m}$ the gyromagnetic factor.

Since the system has a ferromagnetic ground state, the global $z$ direction may be identified with the direction of the magnetization. In the ground state, all the $\hat{S}_i^z$ operators assume their maximal eigenvalue, and since (3.7) conserves the total momentum in the absence of external magnetic field, the system will remain in this state during the time evolution. For the analysis of the low-energy excitations around this ground state, it is useful to introduce the operators

$$\hat{S}^\pm_i = \hat{S}^x_i \pm i \hat{S}^y_i, \quad \text{(3.8)}$$

$$\left[ \hat{S}^z_i, \hat{S}^\pm_j \right] = \pm \delta_{ij} \hat{S}_i^\pm, \quad \text{(3.9)}$$

$$\left[ \hat{S}^+, \hat{S}^-_j \right] = \delta_{ij} 2 \hat{S}^z_i. \quad \text{(3.10)}$$

In the next step, the Holstein–Primakoff transformation[56],

$$\hat{S}_i^z = S - a_i^\dagger a_i, \quad \text{(3.11)}$$

$$\hat{S}_i^+ = \sqrt{2S - a_i^\dagger a_i}, \quad \text{(3.12)}$$

$$\hat{S}_i^- = a_i^\dagger \sqrt{2S - a_i^\dagger a_i}, \quad \text{(3.13)}$$

is used to map the spin operators onto a system of noninteracting bosons,

$$\left[ a_i, a_j^\dagger \right] = \delta_{ij}. \quad \text{(3.14)}$$

Close to the ground state, the occupation of the bosonic states is low, meaning that (3.7) may be expanded in $a_i$ and $a_i^\dagger$ or equivalently, in the powers of $1/S$. This leads to

$$\partial_t a_i = \frac{i}{\hbar} \sum_j S J_{ij} (a_i - a_j), \quad \text{(3.15)}$$

$$\partial_t a_i^\dagger = -\frac{i}{\hbar} \sum_j S J_{ij} \left( a_i^\dagger - a_j^\dagger \right), \quad \text{(3.16)}$$
After introducing the Fourier transforms
\[ a_k = \frac{1}{\sqrt{N}} \sum_i e^{-ikR_i} \alpha_i, \]
\[ J_k = \sum_{i-j} e^{-ik(R_i-R_j)} J_{ij}, \]
where \( N \) is the number of atoms in the system, one obtains the excitation frequencies of magnons,
\[ \hbar \omega_k = S (J_k - J_0). \]

Finally, the energy in this lowest-order approximation may be expressed as
\[ H_{\text{magnon}} = \frac{1}{2} J_0 S^2 + \sum_k \hbar \omega_k a_k^\dagger a_k, \]
that is, a sum over independent harmonic oscillators.

### 3.2 Classical ground state and equation of motion

The classical spin model is obtained from the quantum one in the limit \( S \to \infty \). In the quantum case, the difference between the eigenvalues of the \( S^{\alpha}_i \) operators is 1, irrespective of the value of the quantum number \( S \). However, if we rescale the operators as \( S^{\alpha}_i / S \), the eigenvalues will fall between −1 and 1, while their distances will scale as \( 1/S \). This way, the \( S \to \infty \) limit will correspond to the classical unit vectors \( S^{\alpha}_i \) appearing in the Hamiltonian (3.1).

Finding the ground state of the classical model corresponds to minimizing the energy expression (3.1). Although this procedure can also be carried out in the quantum case, the calculated classical ground state will not necessarily be an eigenstate of the quantum Hamiltonian. When the magnon excitations are calculated around the classical ground state, this causes a negative energy correction to the classical ground state energy due to the commutation relations of the magnon creation and annihilation operators. One of the simplest examples is the two-sublattice antiferromagnet, where the classical model predicts alternating spins between the two sublattices, while the quantum ground state cannot be constructed explicitly. For details see e.g. [57]. Since the energy corrections are of the order \( 1/S \), they disappear in the classical limit. Some special noncollinear ground states, which are impractical to handle within a quantum model, will be discussed in chapter 6.

Since the classical quantities commute, one must find an alternative to (3.3) when constructing the equations of motion. This is performed by introducing the Poisson brackets[58–60]
\[ \{ S^{\alpha}_i, S^{\beta}_j \} = -\frac{\gamma}{M_i} \varepsilon^{\alpha\beta\gamma} \delta_{ij} S^{\gamma}_i; \]
then using the general expression for the classical equation of motion,
\[ \partial_t S^{\alpha}_i = \{ S^{\alpha}_i, H \} = \{ S^{\alpha}_i, S^{\beta}_j \} \frac{\partial H}{\partial S^{\beta}_j} = -\frac{\gamma}{M_i} \varepsilon^{\alpha\beta\gamma} S^{\gamma}_i \frac{\partial H}{\partial S^{\beta}_i}; \]
\[ \partial_t S_i = -\gamma S_i \times B^{\pi}_i, \]
with
\[ B_{i}^{\text{eff}} = -\frac{1}{M_{i}} \frac{\partial H}{\partial \mathbf{S}_{i}}. \] (3.24)

Note that the chain rule in (3.22) can be used for an arbitrary form of the Hamiltonian, since it is a general property of Poisson brackets. In the quantum case, (3.5) only holds for special Hamiltonians which do not contain on-site anisotropy or higher-order terms, since quantum operators do not commute. The ground state is an equilibrium state of the system, meaning that the right-hand side of (3.23) is equal to zero. This implies \( \mathbf{S}_{i} \parallel B_{i}^{\text{eff}} \), which is equivalent to saying that the gradient of the energy expression (3.1) is zero on the configuration space with fixed spin length. We also note that although we arrived at (3.23) using the classical limit of the quantum equation of motion, it can also be derived within adiabatic density functional theory[47].

The calculation of the spectrum of excitations around the ground state relies on an expansion in small quantities. For this purpose we will use a coordinate system where the local \( z \) axis is parallel to the spin direction in the ground state at every lattice site, and the small quantities will correspond to deviations in the perpendicular directions. The algorithm for rotating the spins and the interaction matrices is given explicitly in appendix B.1.

### 3.3 Spin waves

The low-energy excitations around an arbitrary classical ground state can be calculated similarly to how it was done for the quantum ferromagnet in section 3.1. For a quantum Hamiltonian describing a layered system where the spins are all parallel in one layer, but the magnetization direction may change between the layers, this procedure is discussed in detail in [61] and [62]. Here we will largely follow this derivation for the classical model (3.1), but we shall not require that any two spins should be parallel in the ground state.

In the coordinate system where the magnetization in the ground state is parallel to the local \( z \) axis at every lattice point, we will introduce the new variables \( q_{i}, p_{i} \) as
\[ \tilde{S}_{i}^{z} = 1 - \frac{\gamma}{M_{i}} \frac{q_{i}^{2}}{2} - \frac{\gamma}{M_{i}} \frac{p_{i}^{2}}{2}, \] (3.25)
\[ \tilde{S}_{i}^{x} = \sqrt{\frac{\gamma}{M_{i}}} p_{i} \sqrt{1 - \frac{\gamma}{M_{i}} \frac{q_{i}^{2}}{4} - \frac{\gamma}{M_{i}} \frac{p_{i}^{2}}{4}}, \] (3.26)
\[ \tilde{S}_{i}^{y} = \sqrt{1 - \frac{\gamma}{M_{i}} \frac{q_{i}^{2}}{4} - \frac{\gamma}{M_{i}} \frac{p_{i}^{2}}{4}} \sqrt{\frac{\gamma}{M_{i}}} q_{i}, \] (3.27)

analogously to the Holstein–Primakoff transformation (3.11)-(3.13). The new variables, describing the small deviations from the ground state, admit the canonical Poisson brackets of the coordinate and momentum,
\[ \{ q_{i}, p_{j} \} = \delta_{ij}, \] (3.28)
as well as the equations of motion,

\[
\partial_t q_i = \frac{\partial H}{\partial p_i},
\]

\[
\partial_t p_i = -\frac{\partial H}{\partial q_i}.
\]

In these new variables, the spin waves basically correspond to the normal modes of the classical mechanical system. The Hamiltonian may be expanded around the ground state up to second-order terms in \( q_i, p_i \) as

\[
H_{SW} = E_0 + \frac{1}{2} \begin{bmatrix} q^T & p^T \end{bmatrix} \begin{bmatrix} C & B^T \\ B & A \end{bmatrix} \begin{bmatrix} q \\ p \end{bmatrix},
\]

where \( q = \{q_i, i = 1, \ldots, N\}, p = \{p_i, i = 1, \ldots, N\} \) are coordinate and momentum vectors.

For the Hamiltonian (3.1), the elements of the matrices \( A, B, C \) are defined as

\[
A_{ij} = \frac{\gamma}{\sqrt{M_iM_j}} \tilde{j}_{ij}^{xx} - \delta_{ij} \sum_k \frac{\gamma}{\sqrt{M_iM_k}} \tilde{j}_{ik}^{xx} - \delta_{ij} \frac{\gamma}{M_i} 2 \tilde{K}_{ii}^{xx} + \delta_{ij} \gamma \tilde{B}_i^x,
\]

\[
C_{ij} = \frac{\gamma}{\sqrt{M_iM_j}} \tilde{j}_{ij}^{yy} - \delta_{ij} \sum_k \frac{\gamma}{\sqrt{M_iM_k}} \tilde{j}_{ik}^{yy} - \delta_{ij} \frac{\gamma}{M_i} 2 \tilde{K}_{ii}^{yy} + \delta_{ij} \gamma \tilde{B}_i^y,
\]

\[
B_{ij} = \frac{\gamma}{\sqrt{M_iM_j}} \tilde{j}_{ij}^{xy} + \delta_{ij} \frac{\gamma}{M_i} 2 \tilde{K}_{ii}^{xy},
\]

where the tilde denotes that the coupling coefficients are written in the rotated local coordinate system – see appendix B.1 for the exact definition. During the second-order approximation, we drop the upper limit

\[
q_i^2 + p_i^2 \leq \frac{4M_i}{\gamma}
\]

on the magnitude of the variables – see (3.26)-(3.27). This is analogous to the quantum case, where the limit 2S on the bosonic occupation numbers (3.12)-(3.13) is no longer required in (3.20). At high temperature, where the thermal expectation value of the squared deviations becomes comparable to the limit (3.35), spin wave theory is no longer applicable, since the fluctuations destroy the ordered ground state of the system.

The equation of motion reads

\[
\partial_t \begin{bmatrix} q \\ p \end{bmatrix} = \begin{bmatrix} B & A \\ -C & -B^T \end{bmatrix} \begin{bmatrix} q \\ p \end{bmatrix}.
\]

Note that the linear term in the expansion (3.31) must disappear around the ground state, otherwise the equation of motion would not equal zero in the point around which the expansion is carried out, \( q_i = p_i = 0 \).

Similarly to the quantum case, it is possible to introduce the variables \( a_{k\tau}, k = 1, \ldots, N \) satisfying the Poisson brackets

\[
\{a_{k\tau}, a_{k'\tau'}^*\} = -i\delta_{kk'}. 
\]
which means that they correspond to the classical equivalents of the bosonic operators. The equation of motion (3.36) becomes diagonal in the new observables,

\begin{align}
\partial_t a_{k\uparrow} &= -i \omega_k a_{k\uparrow}, \\
\partial_t a^*_{k\downarrow} &= i \omega_k a^*_{k\downarrow},
\end{align}

(3.38) \quad (3.39)

with \( \omega_k \geq 0 \).

This also means that the Hamiltonian generating the equations of motion may be written in the form

\[ H_{SW} = E_0 + \sum_k \omega_k a^*_{k\downarrow} a_{k\uparrow}. \]

(3.40)

The proof for the existence of the matrix transformation yielding (3.37)-(3.40) is given in appendix B.2.

The spin wave frequencies \( \omega_k \) play a crucial role in further theoretical tools and results presented in this thesis. They are required for the perturbative treatment of the Hamiltonian introduced in chapter 4. They encode information about the difference between ferromagnetic, spin spiral and skyrmion lattice phases discussed in chapter 6. It is possible to calculate them from numerical simulations; an example is given in chapter 8. Finally, they can be used to determine the characteristic timescales in the system, which influence the time step in the numerical solution of the spin dynamical equations; see section 12.1 for a more detailed discussion.
Chapter 4

Finite-temperature methods

In this chapter we will discuss theoretical methods applicable for the inclusion of finite-temperature effects in classical spin systems described by the Hamiltonian (3.1). They can explain the softening of the spin wave energies at elevated temperatures, as well as possible phase transitions as a function of temperature.

4.1 Spin wave frequencies at finite temperature from perturbation theory

The methodology discussed in chapter 3 is only applicable for determining the spin wave frequencies at zero temperature. At finite temperature, the spins are no longer confined to a given direction as in the ferromagnetic ground state. Instead they may be characterized by the time-averaged magnetization, which decreases with increasing temperature, and disappears in the paramagnetic phase. The decrease of the magnetization will lead to a similar decrement in the spin wave frequencies.

In (3.31), the Hamiltonian (3.1) was expanded around the ground state in the canonical \( q_i, p_i \) variables up to second-order terms. If the system is coupled to a heat bath at finite temperature, the equilibrium properties are characterized by the free energy rather than the expectation value of the Hamiltonian. In the case of the quadratic expression (3.40), the free energy can be calculated analytically,

\[
e^{-\frac{1}{k_B T}} F_{SW} = \int e^{-\frac{1}{k_B T} \left( E_0 + \sum_k \omega_k a_k^\dagger a_k \right)} \prod_k d\text{Re} a_k^\dagger d\text{Im} a_k^\dagger = e^{-\beta E_0} \prod_k \frac{\pi k_B T}{\omega_k}, \quad (4.1)
\]

\[
F_{SW} = E_0 - N k_B T \ln \pi - N k_B T \ln k_B T + k_B T \sum_k \ln \omega_k, \quad (4.2)
\]

Another interpretation of (4.2) is based on introducing the occupation numbers and entropy of spin waves. Since (3.40) is the sum of independent harmonic oscillators, the expectation values of the products of two observables read

\[
\langle a_k^\dagger a_k^\dagger \rangle_{SW} = \delta_{kk'} n_k, \quad (4.3)
\]
\[
\langle a_k^\dagger a_k \rangle_{SW} = \langle a_k^\dagger a_k^\dagger \rangle_{SW} = 0, \quad (4.4)
\]

where \( \langle \rangle_{SW} \) denotes expectation value with respect to the spin wave Hamiltonian (3.40). The spin wave occupation number in (4.3) takes the form

\[
n_k = \frac{k_B T}{\omega_k}, \quad (4.5)
\]
the classical analogue of the Bose function.

Inserting (4.5) into (4.2) leads to

\[ F_{SW} = E_0 + \sum_k \omega_k n_k - TS + C(T), \]

(4.6)

where the spin wave entropy \( S \) may be expressed as

\[ S = k_B \sum_k \ln n_k, \]

(4.7)

as is usual for classical particles described by the Boltzmann distribution. The constant \( C(T) \) in (4.6) does not depend on the \( E_0, \omega_k \) system parameters, and therefore will be dropped from further calculations. Note that in the classical case, the temperature correction to the expectation value of the energy, \( \sum_k \omega_k n_k = Nk_B T \), does not depend on the system parameters explicitly, either; nevertheless, we will keep this term to emphasize the analogy with the quantum case, and because it will play an important role in the variational method discussed below.

The original Hamiltonian (3.1) may be expanded up to higher-order terms in the variables \( q_i, p_i \) using (3.25)-(3.27). These higher-order terms will be handled by standard perturbation methods from field theory – see e.g. [63]. In first order of the perturbation series, the free energy (4.6) is modified as

\[ F = E_0 + \sum_k \omega_k n_k - k_B T \sum_k \ln n_k + \langle H_1 \rangle_{SW}, \]

(4.8)

where \( H_1 \) contains the higher-order terms. Since (3.40) has a Gaussian form, all higher-order expectation values will simply reduce to a product of pairwise expectation values as in (4.3)-(4.4), and one has to perform a summation over the products of all possible pairs, according to Wick’s theorem. If \( H_1 \) is truncated at quartic terms, (4.8) will read

\[ F = E_0 + \sum_k \omega_k n_k + \frac{1}{2} \sum_{k,k'} P_{kk'} n_k n_{k'} - k_B T \sum_k \ln n_k. \]

(4.9)

The matrix \( P_{kk'} \) can chosen to be symmetric, since it is multiplied by a quantity symmetric in \( k, k' \). \( P_{kk'} \) may only be determined numerically in most cases – see appendix B.2.

Finite-order corrections to the free energy such as (4.9) will always be analytical in the variables, while phase transitions correspond to singularities in the free energy. The singularities occur as a consequence of summing up the perturbation series. A simple way of summing up perturbative corrections to the free energy, which is easy to generalize to ground states other than the ferromagnetic state, was formulated in [64] for a nearest-neighbour quantum Heisenberg model on the simple cubic lattice. For generalizations to other types of interactions and classical Hamiltonians see e.g. [65, 66]. The basic idea is to treat the \( n_k \) occupation numbers as variables, and minimize the free energy by variation with respect to these parameters, since the actual free energy of the system will always be lower than any form of (4.9) obtained within single-particle perturbation theory. This minimization leads to

\[ n_k = \frac{k_B T}{\omega_k + \sum_{k'} P_{kk'} n_{k'}}, \]

(4.10)
which has to be solved self-consistently. Note that (4.10) is analogous to (4.5) if the
denominator is interpreted as a finite-temperature spin wave frequency,

$$\omega_k (T) = \omega_k + \sum_{k'} P_{kk'} n_{k'}.$$  \hspace{1cm} (4.11)

At zero temperature, all occupation numbers are zero, and (4.11) reduces to the
original spin wave spectrum.

Equation (4.10) can describe a phase transition, since it will only have a solution
below a certain critical temperature $T_c$, at which temperature the spin waves completely
destabilize the system. However, some predictions of the model are incorrect; the most
obvious one is that the magnetization, calculated as the expectation value of $\hat{S}_z$ from
(3.25), will not go to zero at $T_c$ even in the simple ferromagnetic-paramagnetic transition
described in [64]. This means that the model suggests a first-order phase transition
instead of a second-order one.

Relying on Green function methods[67] such as the random phase approximation[68]
solves the discrepancy with the magnetization, and correctly predicts the order of the
phase transition. Similarly to the variational method above, the Green function method
was originally applied to isotropic Heisenberg ferromagnets; for generalizations see e.g.
[69–75]. We will not discuss the Green function methods in this thesis, mainly because
it is complicated to generalize the calculation of the magnetization or order parameter
to general types of interactions and ground states. Another issue is that here we only
treat two-dimensional systems, where long-range order is destroyed at finite temperature
if the spin wave spectrum is gapless due to the spontaneous breaking of a continuous
symmetry, according to the Mermin–Wagner theorem[76]. Green function theory repro-
duces this instability, but when a small gap is introduced in the system by anisotropy
terms or boundary conditions, we found that the critical temperatures obtained from
the variational method are comparable to the predictions of Green function theory, or
are even closer to the values determined from numerical simulations. It is also worth
mentioning that the computational costs of the variational method are lower than those
of Green function theory.

The above described method will be used for determining the spin wave frequencies
at finite temperature in section 8.2.

4.2 Spin wave expansion

During the determination of the spin wave frequencies at zero temperature in sec-
tion 3.3 and at finite temperature in section 4.1, the expansion of the Hamiltonian (3.1)
in the small variables $q_i, p_i$ was carried out around the ground state of the system. How-
ever, we only relied on two assumptions. The first one is discussed after (3.36): the
derivative of the Hamiltonian with respect to the variables must disappear. This char-
acterizes equilibrium states of the system, where the equations of motion (3.29)-(3.30) have
constant zero solutions. The second one is that all spin wave frequencies must be nonneg-
ative $\omega_k \geq 0$, which is connected to the second partial derivatives of the Hamiltonian –
see appendix B.2 for a detailed discussion. Spin configurations satisfying both conditions
are called stable equilibrium states; if the initial state of the system is close to a stable
equilibrium state, it will remain there throughout the time evolution described by the
equations of motion. If relaxation effects are also included, which will be introduced in
section 5.1, the $q_i$ and $p_i$ variables will converge to zero. On the other hand, negative or imaginary spin wave frequencies will repulse the system away from the equilibrium state. Since we are dealing with a many-dimensional configuration space, the system may have multiple stable equilibrium states. The one with the lowest energy is called the ground state, but the other metastable states also correspond to local energy minima. At finite temperature, a metastable state may become more favourable from a free energy standpoint, leading to a first-order phase transition between the ground state and the metastable state.

Spin wave expansion provides a quantitative theoretical description of such a phase transition. It is based on the expression of the free energy in spin wave theory,

$$
\frac{F}{N} = \frac{E_0}{N} + \frac{k_B T}{N} \sum_k \ln \omega_k + C(T),
$$

(4.12)

where $C(T)$ does not depend on the parameters of the equilibrium state $E_0$ and $\omega_k$. Compared to (4.6), the spin wave correction to the expectation value of the energy is also included in the constant $C(T)$.

The expression (4.12) can describe a transition between two different stable equilibrium states specified by the parameters $E_0, \omega_k$ and $E'_0, \omega'_k$. If $E_0 < E'_0$ and the relation $\sum_k \ln \omega_k > \sum_k \ln \omega'_k$ applies, then the system will switch from the first state to the second one at the temperature where the free energies of the two states are equal,

$$
k_{B} T_{\text{trans}} = \frac{E'_0 - E_0}{\sum_k \ln \omega_k - \sum_k \ln \omega'_k}.
$$

(4.13)

The quantum version of this method was applied in [77] and [78] to describe the transition from the ferromagnetic to the spin spiral state in bulk Dy. It should be noted that this method only gives numerically good transition temperatures if the temperature itself is small, since the spin wave expansion for the free energy (4.12) becomes less accurate as the temperature is increased.

The theory discussed above does not give any information about at which temperature the equilibrium states become unstable, and the system transforms into the disordered paramagnetic state. The destabilizing effect of the paramagnetic state can be included in spin wave expansion by the same perturbative method that was discussed in section 4.1. The self-consistency equation (4.10) will only have a solution below a certain critical temperature $T_c$, and this temperature will depend on the considered equilibrium state. We note that calculating the perturbative corrections can become numerically very demanding for noncollinear equilibrium states.

Spin wave expansion will be applied to the description of first-order phase transitions in sections 10.4 and 10.5.

### 4.3 Temperature-driven phase transitions in the mean-field approximation

Besides the theory based on spin wave excitations in section 4.2, phase transitions may also be described within a mean-field model. The theory summarized below can be applied to first- and second-order phase transitions.
The mean-field approximation is obtained by performing the replacement

\[ S_i \to S_i - \langle S_i \rangle + \langle S_i \rangle \]  \hspace{1cm} (4.14)\)

in the interacting part of the Hamiltonian (3.1), and dropping the terms which are quadratic in the quantity \( S_i - \langle S_i \rangle \), justified by the smallness of the fluctuations at low temperature[79]. In the absence of external magnetic field, this leads to the expression

\[ H_{MF} = \sum_{ij} S_i^\alpha J_{ij}^\beta \langle S_j^\beta \rangle - \frac{1}{2} \sum_{ij} \langle S_i^\alpha \rangle J_{ij}^\alpha \langle S_j^\beta \rangle + \sum_i K_i^\alpha \langle S_i^\alpha \rangle = S_i^\beta . \]  \hspace{1cm} (4.15)\)

The first term on the right-hand side of (4.15) can be written as

\[ \sum_{ij} S_i^\alpha J_{ij}^\beta \langle S_j^\beta \rangle = - \sum_i S_i^\alpha B_{i,MF}^\alpha , \]  \hspace{1cm} (4.16)\)

with \( B_{i,MF}^\alpha \) the eponymous mean field at site \( i \), given in energy dimensions. The second term does not depend on the variables \( S_i \), but will play an important role in determining the free energy of the system. It is also important not to perform the replacement (4.14) in the on-site anisotropy term, because this part will be responsible for the occurrence of phase transitions in the model.

Since (4.15) represents a sum over independent spins, the partition function becomes a product of integrals performed over unit spheres,

\[ Z_{MF} = e^{-\frac{1}{k_B T} \sum_{ij} \langle S_i^\alpha \rangle J_{ij}^\beta \langle S_j^\beta \rangle} \prod_i \int e^{-\frac{1}{k_B T} S_i^\alpha \left( \sum_j J_{ij}^\alpha \langle S_j^\beta \rangle + K_i^\alpha \langle S_i^\beta \rangle \right)} dS_i , \]  \hspace{1cm} (4.17)\)

while the free energy reads

\[ F_{MF} = -k_B T \ln Z_{MF} \]

\[ = -\frac{1}{2} \sum_{ij} \langle S_i^\alpha \rangle J_{ij}^\alpha \langle S_j^\beta \rangle - k_B T \sum_i \ln \int e^{-\frac{1}{k_B T} S_i^\alpha \left( \sum_j J_{ij}^\alpha \langle S_j^\beta \rangle + K_i^\alpha \langle S_i^\beta \rangle \right)} dS_i . \]  \hspace{1cm} (4.18)\)

Similarly to the idea behind density functional theory in section 2.1, decreasing the number of integral variables in mean-field theory significantly simplifies the calculations.

The optimal value of the \( \langle S_i^\alpha \rangle \) parameters in the free energy may be obtained by minimizing (4.18) with respect to them – see the discussion after (4.9) in section 4.1. Calculating the first derivative of the free energy with respect to \( \langle S_i^\alpha \rangle \) and setting it equal to zero leads to

\[ \langle S_i^\alpha \rangle = \int S_i^\alpha e^{-\frac{1}{k_B T} S_i^\alpha \left( \sum_j J_{ij}^\alpha \langle S_j^\beta \rangle + K_i^\alpha \langle S_i^\beta \rangle \right)} dS_i \]

\[ \times \left( \int e^{-\frac{1}{k_B T} S_i^\alpha \left( \sum_j J_{ij}^\alpha \langle S_j^\beta \rangle + K_i^\alpha \langle S_i^\beta \rangle \right)} dS_i \right)^{-1} . \]  \hspace{1cm} (4.19)\)

Note that (4.19) may have several solutions which correspond to stable and unstable equilibrium points of the free energy landscape, similarly to how the spin wave expansion was performed around different metastable states in section 4.2. For example, the paramagnetic state \( \langle S_i^\alpha \rangle = 0 \) is always the solution of (4.19), since in this case (4.15) simplifies to the on-site anisotropy term, where all expectation values are zero due to time-reversal
invariance. Therefore, it is necessary to perform a stability analysis of the equilibrium points based on the second-derivative tensor of the free energy[80]. Below the critical temperature, the paramagnetic solution will become unstable with respect to a certain mean-field spin configuration \( \langle S_i^z \rangle \neq 0 \), indicating a transition into the ordered state.

The method is also capable of describing transitions between different ordered states if the mean-field spin configuration changes with temperature, or when the free energy curves of different equilibrium states intersect as in section 4.2. As a model system, we will treat an ultrathin film with ferromagnetic scalar Heisenberg exchange interactions \( J^{zz} = J^{yy} = J < 0 \) with the \( z \) nearest neighbours, as well as on-site \( K^{zz} \) and two-site \( \Delta J = J^{zz} - J^{xx} = J^{zz} - J^{yy} \) anisotropies. We will suppose that the two types of anisotropies prefer different directions. In this case, the easy axis of the system may rotate as a function of temperature; such a phenomenon is known as a spin reorientation transition.

We will identify the \( z \) axis with the out-of-plane direction of the film, and suppose \( \Delta J > 0 \), meaning that the two-site anisotropy prefers an in-plane spin orientation. This is reasonable because the two-site anisotropy term represents a simplified form of the dipolar interaction – see (2.41) –, which is generally included in the description of spin reorientation transitions[79, 81], and always prefers if the spins are located within the plane. Within the mean-field approximation, the dipolar term and the two-site anisotropy have equivalent forms[81], so it is sufficient to consider the latter expression. We can only expect a reorientation transition if the on-site anisotropy competes with the two-site term, meaning \( K^{zz} < 0 \). The spins in the ferromagnetic ground state will be pointing perpendicularly to the plane if such a configuration is energetically preferable to the in-plane one,

\[
K^{zz} + \frac{1}{2}z\Delta J < 0. \tag{4.20}
\]

From the free energy expression (4.18) it can be calculated that the paramagnetic state is stable with respect to the out-of-plane ferromagnetic state \( \langle S_i^z \rangle \neq 0 \) for

\[
k_B T > \frac{1}{3}z(J + \Delta J) - \frac{4}{15}K^{zz}, \tag{4.21}
\]

and with respect to the in-plane ferromagnetic state \( \langle S_i^z \rangle \neq 0 \) for

\[
k_B T > \frac{1}{3}zJ + \frac{2}{15}K^{zz}. \tag{4.22}
\]

For the derivation see appendix B.3. If (4.21) is a stronger restriction than (4.22), then the paramagnetic state will first become unstable towards the out-of-plane ferromagnetic state; the condition for this is

\[
K^{zz} + \frac{5}{6}z\Delta J < 0. \tag{4.23}
\]

The system will remain in this state down to \( T = 0 \), since (4.23) implies (4.20). However, it is possible that the ground state is out-of-plane ferromagnetic – (4.20) holds –, but the paramagnetic state first becomes unstable towards the in-plane ferromagnetic state – (4.23) does not hold. In this case, the system must rotate from the out-of-plane to the in-plane direction as the temperature is increased, since the former one has lower energy, but the latter one has a lower free energy close to \( T_C \).
A more detailed analysis shows that there is no intermediate stable ferromagnetic state in the mean-field description, where the magnetization has both an out-of-plane and an in-plane component. Instead, the system jumps from the out-of-plane to the in-plane direction at a fixed temperature value, characteristic of a first-order spin reorientation transition. We note that considering nonequivalent atoms, such as multiple layers, increases the types of possible phase transitions[81]. For a double-layer, the rotation from the out-of-plane to the in-plane direction may happen continuously as a function of temperature, indicating a second-order transition. For an even larger number of layers, a reversed reorientation transition is also possible; this means going from an in-plane ferromagnetic ground state to an out-of-plane state at higher temperature, as has been demonstrated in [82].

We will apply the method discussed above for the description of various types of spin reorientation transitions in sections 9.3, 9.4 and 10.6.
Chapter 5
The stochastic Landau–Lifshitz–Gilbert equation

In this chapter we will derive the stochastic Landau–Lifshitz–Gilbert equation[35–38], which incorporates dissipation and thermal fluctuation into the canonical equation of motion (3.23) on empirical grounds. Both the dissipation and fluctuation effects are a consequence of the spin–orbit interaction between the localized moments and fast degrees of freedom such as conduction electrons, phonons and nuclear spins. They are encapsulated in the empirical dimensionless Gilbert damping parameter $\alpha$. Many of the results presented in this thesis are obtained from spin dynamics simulations, which correspond to the numerical solution of the stochastic Landau–Lifshitz–Gilbert equation. We shall also derive a form of the equation of motion written in the local coordinate system defined by the vectors $e_i, e_1, e_2$ in section 2.5, and construct appropriate numerical solvers.

5.1 The Landau–Lifshitz–Gilbert equation

The canonical equation of motion (3.23) conserves the energy of the system,

$$\partial_t H = \sum_i \partial_i S_i \frac{\partial H}{\partial S_i} = -\sum_i \partial_i S_i M_i B_i^{\text{eff}} = 0,$$

(5.1)

since $\partial_i S_i$ is perpendicular to $B_i^{\text{eff}}$. Although this is in agreement with the results of classical electrodynamics such as Larmor precession of magnetic moments around an external field, magnetic solids do not follow this description. The magnetic moment of isotropic materials rotates until it becomes parallel to the external field, thereby minimizing the energy. This effect also applies microscopically, for example when aligning the spins parallel in a ferromagnetic material at low temperature. To include this effect, Landau and Lifshitz[35] proposed an equation of the form

$$\partial_t S_i = -\gamma S_i \times B_i^{\text{eff}} - \lambda \gamma S_i \times (S_i \times B_i^{\text{eff}}),$$

(5.2)

with the dimensionless damping parameter $\lambda$. Gilbert[36] suggested using the equation of motion

$$\partial_t S_i = -\gamma S_i \times B_i^{\text{eff}} + \alpha S_i \times \partial_t S_i,$$

(5.3)

which after expressing $\partial_t S_i$ transforms into

$$\partial_t S_i = -\gamma' S_i \times B_i^{\text{eff}} - \alpha' S_i \times (S_i \times B_i^{\text{eff}}).$$

(5.4)
This is equivalent to (5.2) apart from the fact that the gyromagnetic factor is also renormalized as $\gamma' = \frac{\gamma}{1 + \alpha^2}$. The advantage of the Gilbert form is that the speed of the relaxation will not increase unboundedly in the high-damping limit, improving numerical stability. In the following, we will use the form (5.4) and refer to the dimensionless damping parameter $\alpha$ as the Gilbert damping. The components of the torque in (5.4) leading to precession and relaxation are illustrated in figure 5.1.

During the time evolution described by (5.4), the energy of the system will follow

$$\partial_t H = \sum_i \partial_t S_i \frac{\partial H}{\partial S_i} = -\alpha \gamma' \sum_i M_i \left[ (B^\text{eff}_i)^2 - (S_i B^\text{eff}_i)^2 \right],$$

that is, it will monotonically decrease until the spin at every lattice point is parallel to $B^\text{eff}_i$. As discussed in section 3.2, this corresponds to an energy minimum of the system. On the other hand, the length of the spins is conserved during the time evolution since $\partial_t S_i$ is perpendicular to $S_i$, meaning that this model still only allows for transversal spin fluctuations, in agreement with the ab initio calculations in section 2.5.

Generally, we will consider 3d magnetic atoms in this thesis where the spin–orbit interaction is weak, and consequently $\alpha$ is small ($\alpha \leq 0.1$). We note that $\alpha$ may also be calculated using ab initio methods[83], which leads to comparable values of the damping as the ones used here. Equation (5.5) indicates that the relaxation is fastest for $\alpha = 1$, which is important when numerically determining the ground state of the system.

### 5.2 The stochastic Landau–Lifshitz–Gilbert equation

Although the Landau–Lifshitz–Gilbert equation (5.4) converges towards an energy minimum, at finite temperature the system instead should converge to the equilibrium Boltzmann distribution, since the solid acts as a heat bath for the spin system through interactions with conduction electrons and phonons. To achieve such an equilibrium distribution, the spin system must be described by a stochastic rather than a deterministic differential equation. Such an equation of motion was first proposed by Brown[37],

$$\partial_t S_i = -\gamma' S_i \times (B^\text{eff}_i + B^\text{th}_i) - \alpha \gamma' S_i \times (S_i \times (B^\text{eff}_i + B^\text{th}_i)), \quad (5.6)$$
where $B_i^{th}$ describes the interaction with the heat bath, and thus is the only term that depends on the temperature of the environment. As will be discussed below, describing this interaction does not necessitate the introduction of further empirical coefficients beyond the Gilbert damping. We note that Kubo and Hashitsume\cite{38} proposed a similar model to (5.6), the difference being that the thermal field $B_i^{th}$ is only added to the precession term. Since this modification only changes further calculations by $1 + \alpha^2$ factors, we will only consider Brown’s version of the equation in the following, just as we chose the Gilbert form (5.4) over the Landau–Lifshitz equation (5.2).

Since the interaction with the heat bath consists of many small events on a very short timescale, one can assume that the thermal field $B_i^{th}$ is proportional to the Gaussian white noise,

$$B_i^{th} (t) = \sqrt{2D_i} \circ \eta_i (t).$$  \hspace{1cm} (5.7)

The white noise is designated this way since it has zero expectation value,

$$\langle \eta_i^\alpha (t) \rangle = 0,$$  \hspace{1cm} (5.8)

and it is completely uncorrelated in space, time and Cartesian indices,

$$\langle \eta_i^\alpha (t) \eta_j^\beta (t') \rangle = \delta_{ij} \delta^{\alpha\beta} \delta (t - t').$$  \hspace{1cm} (5.9)

The $\circ$ notation in (5.7) indicates that the so-called Stratonovich interpretation of the stochastic differential equation is used during the solution\cite{84}. Ordinary chain rule holds for the Stratonovich form; by multiplying (5.6) with $S_i$ we get

$$S_i \partial_t S_i = \frac{1}{2} \partial_t S_i^2 = 0,$$  \hspace{1cm} (5.10)

meaning that the length of the spin vectors is conserved, in agreement with the applied spin model (3.1). Actual physical processes generally have finite correlation time, meaning that they should be described by some sort of coloured noise instead of the white noise in (5.7); however, mathematical methods for the solution of stochastic differential equations are primarily developed for the white noise or Brownian motion. The Stratonovich interpretation of the stochastic differential equation may be thought of as a limit of coloured noise as the correlation time approaches zero\cite{84}.

The variance $D_i$ of the thermal noise $B_i^{th}$ in (5.7) depends on the temperature of the system, and it can be calculated from the Fokker–Planck equation of (5.6). The Fokker–Planck equation is a deterministic partial differential equation describing the time evolution of the probability density function $P (y, t; x)$, which corresponds to the probability of finding the system in the configuration $y = \{S_i^j\}$ at time $t$, when the system is initialized in the configuration $x = \{S_i^j\}$ at time $t = t_0$. It has the general form

$$\partial_t P (y, t; x) = A^\dagger P (y, t; x),$$  \hspace{1cm} (5.11)

where the operator $A^\dagger$ can be calculated from the stochastic differential equation (5.6); the derivation is presented in appendix C.1. After introducing the spherical coordinates

$$S_i^\theta = \sin \vartheta_i \cos \varphi_i,$$  \hspace{1cm} (5.12)

$$S_i^\varphi = \sin \vartheta_i \sin \varphi_i,$$  \hspace{1cm} (5.13)

$$S_i^\psi = \cos \vartheta_i,$$  \hspace{1cm} (5.14)
the operator is given by
\[ A^i P = \gamma' \left[ \frac{1}{\sin \vartheta_i} \frac{\partial}{\partial \vartheta_i} \left( \frac{\partial H}{\partial \varphi_i} + \alpha \sin \vartheta_i \frac{\partial H}{\partial \vartheta_i} \right) P + \frac{\partial}{\partial \varphi_i} \left( -\frac{1}{\sin \vartheta_i} \frac{\partial H}{\partial \vartheta_i} + \alpha \frac{1}{\sin^2 \vartheta_i} \frac{\partial H}{\partial \varphi_i} \right) P \right] + D_i \gamma'^2 (1 + \alpha^2) \Delta_i P, \] (5.15)
with
\[ \Delta_i = \frac{\partial^2}{\partial \vartheta_i^2} + \cot \vartheta_i \frac{\partial}{\partial \vartheta_i} + \frac{1}{\sin^2 \vartheta_i} \frac{\partial^2}{\partial \varphi_i^2}, \] (5.16)
the Laplacian on the unit sphere.

It is easy to prove[84] by substitution that the Boltzmann distribution
\[ P(y, t; x) = e^{-\frac{1}{\gamma M_i} H(y)} \] (5.17)
is a stationary solution of (5.11) if the variance \( D_i \) of the thermal field satisfies the Einstein relation
\[ D_i = \frac{\alpha k_B T}{\gamma M_i}. \] (5.18)

This result concludes the determination of all parameters in the equation of motion (5.6).

5.3 Numerical solution

The stochastic Landau–Lifshitz–Gilbert equation (5.6), or the corresponding Fokker–Planck equation (5.11) for the probability density function, generally cannot be solved analytically. Although it is possible to apply certain approximative methods in the calculations[37, 85], the most reliable procedure is the numerical solution of the differential equation. The basic definitions of the numerical solution of stochastic differential equations are summarized in appendix C.3.

In this thesis, we will use the so-called semi-implicit B method for the solution of the stochastic Landau–Lifshitz–Gilbert equation (5.6), which was introduced in [86]. The basic idea is that due to the form of (5.6), the increment of the spin vectors \( S_i \) in a single step may be expressed as
\[ S_i(t_{n+1}) = S_i(t_n) + S_i(t_n) \times F_i(t_n), \] (5.19)
where \( F_i(t_n) \) contains the small increments during the time step \( t_{n+1} - t_n = \Delta t \). Instead of (5.19), one can use the approximation
\[ S_i(t_{n+1}) - S_i(t_n) = \frac{1}{2} (S_i(t_n) + S_i(t_{n+1})) \times F_i(t_n), \] (5.20)
where multiplying by \( S_i(t_n) + S_i(t_{n+1}) \) yields \( S_i^2(t_{n+1}) = S_i^2(t_n) \), the conservation of the length of the spin vectors. The method is called semi-implicit since although the right-hand side of (5.20) depends on the value of the spin vectors in the next step \( S_i(t_{n+1}) \), the spin vector can be expressed by solving a set of linear equations, which is simpler than the truly implicit case where \( F_i \) would also depend on \( S_i(t_{n+1}) \).
The semi-implicit B scheme is a so-called predictor-corrector method which calculates $S_i(t_{n+1})$ in two steps. It can be expressed as

\[ \hat{B}_i = -\frac{1}{4'} \left[ \left( B_i^{\text{eff}}(\{S_i(t_n)\}) \right) \hat{J}_{(0)} + \sqrt{2D_i} \hat{J}_{(1)} \right] \]

\[ + \alpha S_i(t_n) \times \left( B_i^{\text{eff}}(\{S_i(t_n)\}) \right) \hat{J}_{(0)} + \sqrt{2D_i} \hat{J}_{(1)} \right], \]  

(5.21)

\[ \hat{A}_i = S_i(t_n) + S_i(t_n) \times \hat{B}_i, \]

(5.22)

\[ \hat{S}_i = \frac{\hat{A}_i + \hat{A}_i \times \hat{B}_i + (\hat{A}_i \hat{B}_i) \hat{B}_i}{1 + \hat{B}_i^2}, \]

(5.23)

\[ B_i = -\frac{1}{2} \gamma' \left[ B_i^{\text{eff}}(\{\hat{S}_i\}) \right] \hat{J}_{(0)} + \sqrt{2D_i} \hat{J}_{(1)} \]

\[ + \alpha \hat{S}_i \times \left( B_i^{\text{eff}}(\{\hat{S}_i\}) \right) \hat{J}_{(0)} + \sqrt{2D_i} \hat{J}_{(1)} \right], \]

(5.24)

\[ A_i = S_i(t_n) + S_i(t_n) \times B_i, \]

(5.25)

\[ S_i(t_{n+1}) = \frac{A_i + A_i \times B_i + (A_i B_i) B_i}{1 + B_i^2}. \]

(5.26)

In (5.21)-(5.26) we have used the notations $\hat{J}_{(0)} = \Delta t$ and $\hat{J}_{n+1} = \sqrt{\Delta t} \xi_{i,n}$, where the $\xi_{i,n}$ standard normal variables are independent in Cartesian and site indices, as well as for different time steps. The symbols $\hat{J}_{(0)}$ and $\hat{J}_{n+1}$ reflect that the expressions represent approximations of certain elementary stochastic integrals – see appendix C.3. The steps (5.23) and (5.26) are responsible for conserving the length of the spins. Equation (5.26) also gives an explicit expression for $S_i(t_{n+1})$, in contrast to the original formulation of the method in [86] where it is truly semi-implicit. We note that $\hat{S}_i$ gives a first approximation for $S_i(t_{n+1})$ instead of $S_i(t_{n+1})$; this is the reason for the smaller rotation in (5.21) compared to (5.24).

The advantage of the semi-implicit B method emphasized in [86] is that it remains stable for relatively large time steps; up to only four steps per precession period are required for the simulations. Following the definition given in appendix C.3, its order of weak convergence is $\beta = 1$, which is the minimal value for methods that are actually convergent. However, its deterministic limit is a second-order convergent method.

The improved stability of the semi-implicit B scheme compared to standard methods described in appendix C.3 is attributed to its conservation properties for $\alpha = 0$ or for a special form of the Hamiltonian (3.1) in [86]. This is similar to how symplectic integrators for classical mechanical systems show better performance than common numerical integration methods for deterministic differential equations.

### 5.4 Local coordinate system

In case of cluster calculations, we used a different form of the stochastic Landau–Lifshitz–Gilbert equation. As discussed in section 2.5, in the *ab initio* calculations we used a local coordinate system at every lattice point, consisting of the orthogonal vectors $e_i$, $e_{1i}$ and $e_{2i}$. In this case, the directions of the exchange-correlation fields $e_i$ were identified with the classical unit vectors $S_i$, and the model Hamiltonian $H$ (3.1) was
replaced by the band energy $E_{\text{band}}$ (2.33). A significant difference between $E_{\text{band}}$ and $H$ is that the explicit form of the former is not known as a function of the $S_i$ variables, which also means that $E_{\text{band}}$ naturally includes higher-order interactions omitted from (3.1).

The stochastic Landau–Lifshitz–Gilbert equation (5.6) may be rewritten in the local coordinate system as

$$
\begin{align*}
\frac{d\beta_{2i}}{dt} &= \frac{\gamma'}{M_i} \frac{\partial E_{\text{band}}}{\partial \beta_{2i}} dt - \frac{\gamma'}{M_i} \frac{\partial E_{\text{band}}}{\partial \beta_{1i}} dt \\
&+ \gamma' \sqrt{2D} e_{2i} \circ dW_i + \alpha \gamma' \sqrt{2D} e_{1i} \circ dW_i, \\
\frac{d\beta_{1i}}{dt} &= - \frac{\gamma'}{M_i} \frac{\partial E_{\text{band}}}{\partial \beta_{1i}} dt - \frac{\gamma'}{M_i} \frac{\partial E_{\text{band}}}{\partial \beta_{2i}} dt \\
&+ \gamma' \sqrt{2D} e_{1i} \circ dW_i - \alpha \gamma' \sqrt{2D} e_{2i} \circ dW_i,
\end{align*}
$$

(5.27)
(5.28)

where the derivatives are given by equation (2.34), meaning that the band energy itself need not be calculated during the solution of the equation of motion. Since the infinitesimal rotations are always perpendicular to the direction of $S_i$, the vector equation (5.6) could be replaced by two scalar equations (5.27)-(5.28). These two equations must be accompanied by

$$
\begin{align*}
\frac{dS_i}{dt} &= - \frac{d\beta_{1i}}{dt} e_{2i} + \frac{d\beta_{2i}}{dt} e_{1i}, \\
\frac{de_{2i}}{dt} &= \frac{d\beta_{1i}}{dt} S_i, \\
\frac{de_{1i}}{dt} &= - \frac{d\beta_{2i}}{dt} S_i.
\end{align*}
$$

(5.29)
(5.30)
(5.31)

which describe how the axes of the local coordinate system are rotated during the time evolution. The infinitesimal Wiener process $dW_i$ in (5.27)-(5.28) is connected to the white noise $\eta_i$ in (5.7); the exact definition is given in appendix C.1.

Since the spin dynamics calculations for magnetic clusters have to be performed in the local coordinate system according to (5.27)-(5.28), we had to implement appropriate stochastic numerical solvers. These solvers must be stable up to relatively large time steps, and they should conserve the length of the spin vectors. We constructed three different numerical solvers with equidistant time step $\Delta t$; the main characteristics of the algorithms are discussed in this section, while their explicit form is given in appendix C.4.

The good stability properties of the semi-implicit B method in section 5.3 have been demonstrated in [86]. Therefore, we first implemented this method in the local coordinate system. It only requires the calculation of the first derivatives (2.34), and uses an intermediate step $\dot{S}_i$, because it is a predictor-corrector method. It may be illustrated by the diagram

$$
\begin{align*}
S_i(t_n) \rightarrow \frac{\partial E_{\text{band}}}{\partial \beta_{ri}} \rightarrow \dot{S}_i \rightarrow \frac{\partial E_{\text{band}}}{\partial \beta_{ri}} \rightarrow S_i(t_{n+1}).
\end{align*}
$$

(5.32)

Due to the presence of the intermediate spin configuration, this method will be referred to as the two-step scheme in the following. Similarly to its counterpart in the global coordinate system, this method has weak order of convergence $\beta = 1$.

For every spin configuration $S_i$, the matrix of the scattering path operator $\tau$ has to be calculated to determine the derivatives (2.34) appearing in the numerical solver. This consumes significantly more computer time than performing the numerical integration of the equation of motion. Since the two-step scheme requires the calculation of $\tau$ during
every time step twice, in the local coordinate system it may actually be preferable to use a one-step scheme, even if the numerical integration step is more complicated than in the two-step scheme. The method requires the calculation of the second derivatives (2.35); it is illustrated by

\[ S_i(t_n) \rightarrow \frac{\partial E_{\text{band}}}{\partial \beta_{ri}}, \frac{\partial^2 E_{\text{band}}}{\partial \beta_{ri} \partial \beta_{pj}} \rightarrow S_i(t_{n+1}). \]  

(5.33)

Despite its more complicated form – see appendix C.4 –, the one-step scheme actually requires less computation time for a single time step, since \( \tau \) is calculated only once. This method has the same order of convergence as the semi-implicit B scheme, namely second order in the deterministic limit and weak order \( \beta = 1 \) in the stochastic case.

Finally, we also implemented a simplified version of the one-step scheme, where only the first derivatives of the band energy (2.34) are used, and the numerical integration step takes less computation time. It is illustrated by

\[ S_i(t_n) \rightarrow \frac{\partial E_{\text{band}}}{\partial \beta_{ri}} \rightarrow S_i(t_{n+1}). \]  

(5.34)

The simplified one-step scheme is weakly convergent with order \( \beta = 1 \), but in contrast to the one-step and two-step schemes, it is only a first-order method in the deterministic limit.

The performance of the numerical solvers is compared to each other on a model system in section 12.1. Although the simplified one-step scheme is faster during a single time step than the other two methods, it will be demonstrated that it requires a 100 times smaller time step to remain stable; therefore, its total computation cost is still higher than that of the one-step scheme for simulating a time interval of fixed length.

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Chapter 6

Noncollinear ground states

In this chapter we will describe the specifics of noncollinear ground states found in spin systems, namely spin spirals and skyrmion lattices. In these spin configurations, the spins are no longer parallel to each other as in the ferromagnetic state, but they are pointing in all directions on a unit circle or a unit sphere for spin spirals and skyrmions, respectively. As it has been alluded to in section 3.2, the description of such states within a quantum model is complicated, since these configurations generally do not represent eigenstates of the quantum Hamiltonian. Here we will discuss the ground states and the spin wave spectra within the classical model. This chapter also serves as a tool for familiarizing oneself with the terminology of spin spirals and skyrmions, which will be used throughout chapters 9-12.

6.1 Planar spin spiral states

Let us consider an ultrathin film in the xy plane. A spin spiral configuration is given by

\[ S_i = (0, \sin (k_0 R_i), \cos (k_0 R_i)) , \]  

(6.1)

In the state described by (6.1), all the spins are confined to the yz plane, and their direction is rotating when moving along the spin spiral wave vector \( k_0 \).

Spin spirals are classified based on the relative orientation of the wave vector and the plane of rotation. The latter can be characterized by the chirality vector \( \chi = S_i \times S_j \), where \( S_i \) and \( S_j \) are neighbouring atoms in the lattice such that \( k_0 (R_j - R_i) > 0 \). If \( k_0 \) and \( \chi \) are perpendicular to each other, the spin spiral is called a cycloidal one; in the case \( k_0 \| \chi \), a helicoidal spin spiral is present in the system.

In this chapter, we will consider spin spiral states created by the Dzyaloshinsky–Moriya interaction. Note that the frustration of the scalar Heisenberg exchange interactions may also lead to the formation of a spin spiral order, as has been observed in the rare-earth magnets Dy and Tb[87], where the Dzyaloshinsky–Moriya interaction is absent. The direction of the Dzyaloshinsky–Moriya vectors is determined by the symmetry of the lattice[53]. As is apparent from the form (2.38) in section 2.6, the Dzyaloshinsky–Moriya interaction prefers if the spins are located in the plane perpendicular to the \( D_{ij} \) vector, meaning that the symmetry also dictates the choice between cycloidal and helicoidal rotations.

The Dzyaloshinsky–Moriya vectors between spins in a two-dimensional lattice are illustrated in figure 6.1. The three-dimensional \( C_{nv} \) and \( D_n \) symmetry point groups
take into account the other layers above and below the considered square lattice. Both
symmetry classes contain a $C_n$ rotation axis perpendicularly to the plane. In the $C_{nv}$
group, there are $n$ further symmetry planes which contain this rotational axis, denoted
by $\sigma_v$ in figure 6.1(a). Since these symmetry planes contain the nearest neighbours,
the Dzyaloshinsky–Moriya vector between them must be perpendicular to the symmetry
plane[53]. Such Dzyaloshinsky–Moriya vectors prefer cycloidal spin spirals[22]. The $C_{nv}$
symmetry group in figure 6.1(a) is obtained by cutting a bcc or fcc lattice perpendicular to
the [100] crystallographic direction and forming a surface. Since in this thesis we consider
ultrathin films and clusters on the surfaces of cubic lattices, the Dzyaloshinsky–Moriya
interaction will favour a cycloidal rotation in all examples presented in chapters 9-12.

The $D_n$ group contains $n$ twofold rotation axes, denoted by $C_2$ in figure 6.1(b), in
the plane perpendicular to the main axis. Since the rotation axes contain the nearest
neighbours, the Dzyaloshinsky–Moriya vectors must be parallel to them[53], preferring
helicoidal spin spirals[22]. Naturally, such rotation axes cannot be present in ultrathin
film systems, since the rotation would switch the bulk and the vacuum regions; instead,
they are common in bulk systems lacking inversion symmetry, a prominent example of
which are B20 materials where magnetic skyrmions have first been identified[11].

The Dzyaloshinsky–Moriya interaction not only chooses a preferred plane for the
spins, but also the rotational sense of the spiral, illustrated in figure 6.2. If we introduce
$\mathbf{n}$ as the normal vector pointing outwards from the surface, then a cycloidal spin spiral
is called right-rotating if the vectors $(\mathbf{k}_0, \chi, \mathbf{n})$ form a right-handed coordinate system;
otherwise it is called left-rotating. This definition of rotational sense is unambiguous in
the cycloidal case, since these three vectors are pairwise perpendicular to each other. In
the case of ultrathin films, the $\mathbf{k}_0$ and $\mathbf{n}$ vectors are by definition perpendicular, but the
vector $\chi$ may be parallel to one of them for general rotational planes. For helicoidal
spirals where $\chi$ and $\mathbf{k}_0$ are parallel to each other, one has to rely on a different definition of
rotational sense as shown in [88].

Figure 6.1: Sketch of nearest-neighbour Dzyaloshinsky–Moriya vectors between atoms in
a single plane, where the three-dimensional point group of the system is (a) $C_{nv}$ or (b) $D_n$.
Blue circles represent atoms in the magnetic layer, while red and orange circles correspond
to atoms in the layers below and above the blue atoms, respectively. $\sigma_v$ denotes a mirror
plane perpendicularly to the surface, while $C_2$ denotes a twofold rotational axis in the
plane.
Figure 6.2: Sketch of (a) right-rotating and (b) left-rotating cycloidal spin spirals. Colour denotes the out-of-plane component of the spins; red is pointing outwards from the surface, while blue is pointing towards the surface.

6.2 Ground state energy and spin wave spectrum of spin spirals

It is also necessary to understand under what circumstances a spin spiral becomes energetically favourable in the system. For this purpose, we will compare a ferromagnetic state and a spin spiral state in the perpendicular plane. The ferromagnetic direction will be preferred by the easy-axis on-site anisotropy $K^{xx} < 0$. We will consider scalar Heisenberg exchange interactions $J_{ij}^{xx} = J_{ij}^{yy} = J_{ij}^{zz} = J_{ij}$, and characterize the Dzyaloshinsky–Moriya vectors by their $x$ component $D_{ij}^{xx} = D_{ij}$, since this is the only component which influences the energy of spin spirals in the $yz$ plane.

Firstly, we introduce the lattice Fourier transforms of the coupling coefficients,

$$
J_k = \sum_{i-j} J_{ij} e^{-ik(R_i - R_j)}, \quad (6.2)
$$

$$
-iD_k = \sum_{i-j} -iD_{ij} e^{-ik(R_i - R_j)}. \quad (6.3)
$$

The $-i$ prefactor in the Dzyaloshinsky–Moriya interaction (6.3) is introduced for convenience; since $D_{ij}$ is antisymmetric in site indices (2.38), its Fourier transform is purely imaginary.

The energy per spin in the ferromagnetic state along the easy axis is

$$
\frac{1}{N} E_{FM} = \frac{1}{2} J_0 + K^{xx}. \quad (6.4)
$$

The spin wave spectrum may be determined from the procedure described in section 3.3. It reads

$$
\omega_k = \frac{\gamma}{M} (J_k - J_0 + iD_k - 2K^{xx}); \quad (6.5)
$$

for the derivation see appendix B.4.

The spectrum with model parameters substituted into (6.5) is illustrated in figure 6.3. The scalar Heisenberg exchange interactions are responsible for the well-known quadratic dispersion relation close to the minimum of the spectrum. The on-site anisotropy opens
Figure 6.3: Spin wave spectrum around the ferromagnetic state (6.5) and around the spin spiral state with wave vector $k_0$ (6.10). The spectrum is calculated for a square lattice with nearest-neighbour scalar Heisenberg exchange interaction $J = -1$ and Dzyaloshinsky-Moriya interaction $D = 0.2$. The wave vector minimizing (6.6) is $k_0^y = 0.03 \frac{2\pi}{a}$. The value of the on-site anisotropy is $K^{xx} = -0.025$ in the ferromagnetic state and $K^{xx} = -0.01$ in the spin spiral state.

a gap in the spectrum, as the other three terms in (6.5) disappear at $k = 0$. The Dzyaloshinsky-Moriya interaction shifts the minimum of the dispersion relation away from the $\Gamma$ point in the Brillouin zone, and also decreases the value of this minimum. As it was discussed in detail in section 4.2, only stable equilibrium spin configurations with $\omega_k \geq 0$ are of interest when discussing the ordered magnetic phases of the system. With the above considerations about the spectrum in mind, this means that the Dzyaloshinsky-Moriya interaction tries to destabilize the ferromagnetic ground state, while the presence of the easy axis improves its stability.

The energy per spin in the spin spiral state (6.1) is

$$\frac{1}{N} E_{SS} = \frac{1}{2} J_{k_0} + \frac{1}{2} i D_{k_0}. \quad (6.6)$$

The ground state of the system will be ferromagnetic as long as the energy of the ferromagnetic state (6.4) is lower than that of any spin spiral state (6.6) with wave vector $k_0$. This leads to the inequality

$$\frac{2}{N} (E_{SS} - E_{FM}) = J_{k_0} + i D_{k_0} - J_0 - 2 K^{xx} > 0. \quad (6.7)$$

Note that (6.7) coincides with the $\omega_k \geq 0$ condition in (6.5) that determined the stability of the ferromagnetic state. This means that the ferromagnetic state in the $x$ direction remains stable as long as it is the ground state of the system, but it cannot represent a metastable state when spin spirals are energetically favourable.

To quantify the stability of the spin spiral state itself, it is necessary to calculate the
spin wave spectra. Performing the calculation presented in appendix B.4 results in

\[
C_+ (k; k_0) = \frac{1}{2} [J_{k+k_0} + J_{k-k_0}] - \frac{1}{2} [iD_{k-k_0} - iD_{k+k_0}] - J_{k_0} - iD_{k_0}, \quad (6.8)
\]

\[
C_- (k; k_0) = J_k - J_{k_0} - iD_{k_0} + 2K^{xx}, \quad (6.9)
\]

\[
\omega_{k;k_0} = \frac{\gamma}{M} \sqrt{C_+ (k; k_0) C_- (k; k_0)}. \quad (6.10)
\]

The spectrum given by (6.10) has also been derived in [89, 90], and for bulk systems without Dzyaloshinsky–Moriya interaction already in [77, 91]. It is presented in figure 6.3 with coupling coefficients substituted in from a model Hamiltonian.

The spin spiral state with wave vector \( k_0 \) is only a stable equilibrium state of the system if

\[
C_+ (k; k_0), C_- (k; k_0) \ge 0 \quad (6.11)
\]

for all spin waves indexed by \( k \). The positivity of \( C_+ (k; k_0) \) is easy to prove by analysing the convexity of expressions (6.2)-(6.3) for such wave vectors \( k_0 \) which are energetically favoured by the Dzyaloshinsky–Moriya interaction – see the energy expression (6.6).

Analysing the form of \( C_- (k; k_0) \), it can be seen that it is minimal for \( k = 0 \). Apart from a sign change and a prefactor, \( C_- (k = 0; k_0) \) coincides with the ferromagnetic spectrum (8.1) and the energy difference (6.7). This means that the spin spiral states in the \( yz \) plane and the ferromagnetic state in the direction perpendicular to the plane cannot be stable with the same model parameters. Starting from the ferromagnetic state and decreasing the magnitude of the anisotropy \( K^{xx} \) will transform the system to the spin spiral state with wave vector \( k_0 \) that minimizes (6.6). At the point where the ferromagnetic state and the spin spiral state are energetically degenerate, both states will also change stability, the ferromagnetic state going from stable to unstable and the spin spiral state going from unstable to stable. There is no intermediate stable equilibrium state where the spins all have finite \( x, y \) and \( z \) components, which should indicate a first-order phase transition since the spin configuration changes abruptly at a given point in the phase diagram. However, first-order phase transitions should happen between different stable equilibrium states, but for each value of \( K^{xx} \) apart from the transition point, exactly one of the states is stable. This means that the transition between the ferromagnetic and spin spiral states in this model is a degenerate case of a second-order phase transition. The ground state of the same system is analysed in detail in [92, 93] within a micromagnetic model, and it is shown that this degeneracy is lifted by the presence of an anisotropy in the \( yz \) plane, leading to a second-order phase transition with an intermediate state where the spin configuration is three-dimensional.

The spin wave spectrum around a spin spiral state (6.10) is compared to the spectrum around the ferromagnetic state in the perpendicular direction (6.5) in figure 6.3. The spectrum around the ferromagnetic state is gapped due to the anisotropy, the minimum is shifted from the \( \Gamma \) point due to the Dzyaloshinsky–Moriya interaction, and the spectrum is quadratic around the minimum in \( k \). By comparison, the spin wave spectrum around the spin spiral state is ungapped since \( C_+ (k = 0; k_0) = 0 \), and it is symmetric around the \( k = 0 \) point. The Dzyaloshinsky–Moriya interaction does not induce an asymmetry in the spectrum because it is perpendicular to the plane of the spiral, while it is parallel to the ferromagnetic direction in (6.5). Expanding (6.10) in \( k \) shows that generally the spectrum starts linearly in the wave vector, which is characteristic for antiferromagnetic spin configurations with an ungapped spectrum[57]; the only exception is \( k_0 = 0 \), which
represents a ferromagnetic state along the z direction, leading to a quadratic dispersion relation.

6.3 Anharmonic spin spirals

If the plane of the spin spiral contains the easy axis of the system, the equilibrium spiral configuration will differ from (6.1), since the spins will be tilted towards the easy direction. In this section, we will summarize basic properties about anharmonic spirals as in section 6.1; the numerical algorithms for determining the ground state energy and the spin wave spectrum in the lattice model are presented in appendix B.5.

We will suppose an easy-axis anisotropy along the out-of-plane direction z in the yz plane of the spiral. If the anisotropy is sufficiently strong, it may also drive the system into the ferromagnetic state despite the presence of the Dzyaloshinsky–Moriya interaction; the difference compared to the model in section 6.2 is that the plane of the spiral will also contain the ferromagnetic direction. This competition between the anisotropy and the Dzyaloshinsky–Moriya interaction has already been described in [87, 94] using a continuum or micromagnetic model

$$\hat{H} = \int j \left( \frac{d\varphi}{dy} \right)^2 + \hat{D} \frac{d\varphi}{dy} + \hat{K} \sin^2 \varphi \, dy,$$

(6.12)

where φ is the angle from the easy z axis in the yz spiral plane. The angle φ is not only defined at discrete lattice points, but as a function of the continuous variable y. The micromagnetic parameters J, D and K describe the strengths of the scalar Heisenberg exchange, Dzyaloshinsky–Moriya and on-site anisotropy terms, respectively. Note that in the micromagnetic model we have $\hat{J}, \hat{K} > 0$, contrary to the sign convention of the lattice model used in this thesis.

The advantage of the micromagnetic model is that the ground state spin configuration can be determined analytically by minimizing (6.12) with variational methods. Similarly to section 6.2, it turns out that the spin spiral state appears above a critical value of the Dzyaloshinsky–Moriya interaction for fixed $\hat{J}$ and $\hat{K}$,

$$|\hat{D}| > \hat{D}_c = \frac{4}{\pi} \sqrt{\hat{J} \hat{K}}.$$

(6.13)

Slightly above this value, the spiral is heavily distorted, resembling a series of stripes with alternating magnetization along the positive and negative z directions. Below the threshold (6.13) for $\hat{D}$, spin spirals are energetically unfavourable compared to the ferromagnetic state, but oppositely magnetized regions may still appear under experimental conditions. The rotation of the spins by 180° between two such regions is called a domain wall. If the rotational plane coincides with the plane the domain wall is located in, one talks about a Bloch wall, the energetically unfavourable equivalent of a helicoidal spiral. However, if the rotational plane is perpendicular to the plane of the domain wall, a Néel wall is present in the system, which is preferred by Dzyaloshinsky–Moriya vectors of the same symmetry class as the cycloidal spiral. Although the magnetostatic dipolar interaction always prefers the helicoidal rotation of spirals, the threshold value for the Dzyaloshinsky–Moriya interaction for creating Néel domain walls in systems with $C_{nv}$ symmetry is well below the critical value (6.13)[95]. This means that whenever the spin spiral state is the ground state of the system, it will always be of cycloidal type in the
$C_{nv}$ symmetry class[22]. We note that this remains true only if the scalar Heisenberg exchange interactions are not frustrated – see section 10.6 for a counterexample.

Although (6.1) does not describe anharmonic spirals, the wave vector $k_0$ may still be determined from the wavelength $\lambda$, defined as the length on which the phase of the spiral rotates by $2\pi$. If the Fourier transform of the spins is calculated, it will also be finite for integer multiples of the wave vector $k_0$ due to the anharmonicity. The magnitude of the chirality vector $\chi$ will no longer be unambiguous, since the angle between neighbouring spins will not be a constant, but the direction of $\chi$ will be fixed, which is sufficient for the determination of the rotational sense as defined in section 6.1.

Including an anisotropy term in the $yz$ plane will also modify the spin wave frequencies compared to (6.10). However, it will only open a gap for the ferromagnetic state $k_0 = 0$, not for real spin spiral states. This is because although the shape of the spiral will become slightly distorted due to the anisotropy, the spectrum will still include a Goldstone mode[96], since translating the spin spiral along the direction of $k_0$ with less than a full wavelength leads to an energetically degenerate but different spin configuration, corresponding to a continuous $U(1)$ symmetry.

### 6.4 Skyrmion lattices

Originally the skyrmion represented a localized field configuration in nonlinear field theory[97, 98], created by higher-order interactions. Later it was demonstrated in magnetic systems[21, 22] that the Dzyaloshinsky–Moriya interaction may also stabilize cylindrically symmetric spin configurations. These objects are localized in two-dimensional systems, while they extend into tubes towards the third dimension. Analogously to the definition in field theory, these localized noncollinear states are called isolated magnetic skyrmions.

It is known that the magnetostatic dipolar interaction may also create domains in a ferromagnetic system. If the domains assume a cylindrical form, they are designated as magnetic bubbles. The size of magnetic bubbles usually falls into the micrometre range, and they easily collapse in the presence of a magnetic field applied oppositely to the magnetization in the domain. In contrast, magnetic skyrmions are generally nanometre-sized objects with a core that is magnetized oppositely to the ferromagnetic background. It is impossible to collapse isolated skyrmions by external magnetic fields in the continuum description[99]; in lattice models, skyrmions disappear if the size of their core becomes comparable to the lattice constant due to a large applied field or the weakness of the Dzyaloshinsky–Moriya interaction[100].

If the ground state of the system is a planar spin spiral state created by the Dzyaloshinsky–Moriya interaction as discussed in section 6.1, it is possible that a hexagonal lattice of magnetic skyrmions becomes energetically the most favourable state in the presence of an external magnetic field[22]. In three-dimensional systems, the skyrmion tubes align parallel to the direction of the external field; in the ultrathin films discussed in this thesis, the skyrmions are localized in the two-dimensional lattice, and the external field must be oriented perpendicular to the surface to make them energetically more favourable. As the magnetic field is further increased, skyrmions become energetically unfavourable compared to the collinear field-polarized background. This usually happens well below the field where they collapse due to lattice discretization effects; instead, skyrmions are removed from the system at the edges of the sample or as a consequence of thermal
fluctuations, and the ground state of the system becomes homogeneous.

The equilibrium spin configuration and consequently the energy of isolated skyrmions or skyrmion lattices may only be determined numerically even in the continuum limit, while there exist analytical expressions for spin spiral states as mentioned in section 6.2. Due to this complication, we will use spin dynamics simulations to determine the exact configurations and energies, and only summarize guidelines about the properties of skyrmions in this section.

The infinite two-dimensional system may be identified with the unit sphere $S^2$ via a stereographic projection. The generalized classical Heisenberg model used in our calculations corresponds to a mapping to the unit sphere, the configuration space of unit-length spins. This means that the spin configuration $\mathbf{S}$ describes a mapping $S^2 \to S^2$, and such mappings may be characterized by how many times the vector field $\mathbf{S}$ winds around the unit sphere. This integer number of windings is called the topological charge. The topological charge of a spin configuration is zero if all the spins are parallel as in the case of the ferromagnetic or the antiferromagnetic state, and it also disappears when the spins are confined to a plane as in the planar spin spiral state. However, skyrmions are characterized by a finite value of the topological charge. Note that in the simulations we consider a finite lattice with periodic boundary conditions, which can be identified with the torus $T^2$ instead of the unit sphere $S^2$, but the topological charge remains an integer regardless.

In field theory, this quantity can be calculated by an integral over the two-dimensional system in the local $x, y$ Cartesian coordinates\cite{101},

\[
Q = \frac{1}{4\pi} \int \mathbf{S} (\partial_x \mathbf{S} \times \partial_y \mathbf{S}) \, dx \, dy, \tag{6.14}
\]

where $\mathbf{S}$ is the vector field on the unit sphere discussed above. If one introduces the usual polar and azimuthal angles

\[
\mathbf{S}(x, y) = \begin{bmatrix}
\sin \vartheta(x, y) \cos \varphi(x, y) \\
\sin \vartheta(x, y) \sin \varphi(x, y) \\
\cos \vartheta(x, y)
\end{bmatrix}, \tag{6.15}
\]

(6.14) transforms into

\[
Q = \frac{1}{4\pi} \int \sin \vartheta(x, y) \frac{\partial (\vartheta, \varphi)}{\partial (x, y)} \, dx \, dy, \tag{6.16}
\]

with the signed Jacobian determinant

\[
\frac{\partial (\vartheta, \varphi)}{\partial (x, y)} = \partial_x \vartheta \partial_y \varphi - \partial_x \varphi \partial_y \vartheta. \tag{6.17}
\]

Note that (6.16) describes a change of variables to the spherical coordinates, where the integral takes the form of the standard expression of the spherical surface area. This demonstrates that $Q$ counts how many times $\mathbf{S}$ winds around the unit sphere. However, note that the Jacobian determinant (6.17) is a signed quantity, describing the relative orientation of the $x, y$ axes in the two-dimensional system and the $\vartheta, \varphi$ variables on the unit sphere; this means that the topological charge may take both negative and positive values.
Figure 6.4: Sketch of the calculation of the topological charge \( Q \) in a lattice model. Note that the orientation of the lattice points and the spins is the same in part (a), but it is the opposite in part (b), leading to a change of sign in the topological charge.

The correct way of generalizing this quantity to the lattice model discussed in this thesis is defined in [102]. The lattice must be partitioned into nearest-neighbour triangles of spins, and one must sum up the signed areas of the spherical triangles spanned by the \( S_i \) vectors. This algorithm is illustrated in figure 6.4. The spin vectors are denoted by \( S_1, S_2, S_3 \) following a counterclockwise rotation on the lattice. For a fixed indexing on the lattice, the spins on the unit sphere may form either a counterclockwise or a clockwise triangle, corresponding to positive and negative topological charges, respectively. The sign of the area is given by the sign of the product \( S_1 (S_2 \times S_3) \). If the calculations are performed for a lattice with periodic boundary conditions, one will always return to the same point during the calculation, and the calculated spherical area will always be an integer multiple \( Q \) of the area of the whole sphere, \( 4\pi \). The advantage of this calculation method is that it minimizes discretization errors: the fluctuations in the topological charge at finite temperature will always correspond to actual topological changes, making it possible to calculate the skyrmion lifetime.

The connection between the topological charge \( Q \) and the number of skyrmions is demonstrated in figure 6.5. As discussed above, skyrmions in ultrathin films are stabilized by an external magnetic field \( B \) applied perpendicularly to the surface; at low field values, they transform into elongated structures resembling parts of the spin spiral, which
nevertheless have the same topological charge \([99, 103]\). The spins in the middle of the skyrmion are always directed oppositely to the external magnetic field, either towards (down) or outwards from (up) the surface. The magnetization of the skyrmion is parallel to the direction of the external field, since there are more spins at the outer edge than in the middle; this is the reason why skyrmions gain energy from the Zeeman term, while spin spirals with zero net magnetization do not. Equation (6.14) changes sign under time reversal, corresponding to switching the direction of the spins and the external field, and therefore the upwards and downwards pointing skyrmions have opposite charge.

Another type of spin configuration is illustrated in figure 6.5(c), which will be referred to as an antiskyrmion. The difference between the skyrmion and the antiskyrmion is that when performing a clockwise rotation on the lattice around the centre of the skyrmion, the spins follow this rotation direction in the case of the skyrmion, but they are rotating counterclockwise in the case of an antiskyrmion. This means that skyrmions and antiskyrmions have an opposite topological charge if the orientation of the external magnetic field is the same. Skyrmions and antiskyrmions gain the same energy due to the isotropic Heisenberg coupling and the Zeeman term \([104]\); the energy difference between them is caused by the Dzyaloshinsky–Moriya interaction. As shown in figures 6.5(a)-(b), the rotational sense of the spins is the same for every cross-section of a skyrmion, so skyrmions gain energy due to the chiral interaction. However, the rotational sense in antiskyrmions in figure 6.5(c) may be either left-handed or right-handed depending on the chosen cross-section, meaning that they do not gain energy from the Dzyaloshinsky–Moriya interaction. Note that the topological charge does not depend on the direction of the Dzyaloshinsky–Moriya vectors; skyrmions adapt to the direction of the vectors by changing their rotational sense, but antiskyrmions never gain energy from it.

For small wave vectors, the scalar Heisenberg exchange and the Dzyaloshinsky–Moriya interaction energy contributions are quadratic and linear in the wave vector, respectively\([10]\). Energy minimization yields that the characteristic scale of spin spirals and skyrmion lattices in reciprocal space is given by \(k_0a \approx D/J\), while the energy gain per spin is approximately \(D^2/|J|\), where \(D\) and \(J\) are the effective Dzyaloshinsky–Moriya and scalar Heisenberg exchange interactions, respectively\([105]\). The noncollinear spin structures only gain this energy if they follow the rotational sense specified by the Dzyaloshinsky–Moriya vectors; therefore, the order of the energy difference between a
skyrmion and an antiskyrmion is \( D^2/|J| \). Similarly, the energy gain of the skyrmion compared to the field-polarized state is also due to the Dzyaloshinsky–Moriya interaction, but since the field-polarized state has a higher magnetization, there is a transition between the two states at approximately \( MB \approx D^2/|J| \)[22]. Upwards pointing skyrmions lose the same energy, since their magnetization is opposite to those of downwards pointing skyrmions. To summarize, antiskyrmions are always energetically unfavourable, and upwards pointing skyrmions are also unfavourable in the case of a sufficiently large external field, meaning that there exists a region in the phase diagram where \( Q \) may be identified with the number of downwards pointing skyrmions which form the hexagonal skyrmion lattice state.
Chapter 7

Simulation methods

In this chapter we will summarize the details of the computer simulation programs used in this thesis. We will focus on the input and output parameters here, as the theoretical background was already discussed in chapters 2 and 5. These programs were used to obtain the results presented in chapters 8-12.

7.1 Self-consistent screened Korringa–Kohn–Rostoker calculations

For the \textit{ab initio} calculations we employed the screened Korringa–Kohn–Rostoker method introduced in chapter 2. This theoretical description only uses the type and geometrical position of the considered atoms as physical input parameters. Numerical input parameters include among others the type of potential used in density functional theory, the angular momentum cutoff $l_{\text{max}}$, the shape of the energy contour during integration, as well as the number of energy points in the contour and $k$ points in the Brillouin zone.

The aim of the calculations was finding the ground state potential of the systems self-consistently. This was first performed for the substrate as a bulk system, then the surface layers using the screening method in section 2.3. For small clusters of atoms, we also applied the embedding method. During the calculations, the direction of the exchange-correlation field $e_i$ (2.16) was the same for all geometrically equivalent atoms. For the layered systems this meant that all the $e_i$ vectors in the same layer were pointing in the same direction. We mention that there exist methods which calculate the potential of a layered system self-consistently in a noncollinear magnetic state, see e.g. [106]. In the cluster systems, none of the atoms were considered to be equivalent, and the directions of the $e_i$ vectors were optimized using the method discussed in [52].

For the description of the spin system, we have numerically solved the stochastic Landau–Lifshitz–Gilbert equation (5.6), where the effective magnetic field $B_i^{\text{eff}}$ (3.24) was determined from the self-consistent potential. The method of determining $B_i^{\text{eff}}$ differed between cluster and layer calculations. However, both types of systems utilized the magnitude of the spin magnetic moments $M_i$, calculated from (2.31).

7.2 Cluster spin dynamics simulations

The cluster calculations were implemented within the screened Korringa–Kohn–Rostoker program. We assumed that the directions of the exchange-correlation fields $e_i = S_i$
follow stochastic Landau–Lifshitz–Gilbert dynamics as discussed in section 5.4. Due to the \textit{ab initio} calculation of the torques acting on the spins, all possible interactions between the atoms in the cluster were taken into account. We did not consider the effect of the magnetic moments in the substrate, but we only used nonmagnetic substrates with weak induced moments such as Au during the simulations, suggesting that such effects were probably negligible.

Besides the self-consistent potential, the spin dynamics simulations also require the Gilbert damping \( \alpha \) and the temperature \( T \) as input parameters. We emphasize that the temperature is only applied during the solution of the stochastic Landau–Lifshitz–Gilbert equation, and all electronic structure calculations were performed at zero temperature. The argument for this approximation is the same as for using the adiabatic decoupling\cite{[47]} in section 2.5: since the relevant magnetic interactions are significantly weaker than the electronic energy scales, thermal effects at low temperature play a more important role in the description of magnetic degrees of freedom compared to electronic ones.

Following the time evolution of the spins \( e_i \) in the cluster, we determined the band energy \( (2.33) \) and the average magnetic moment of the cluster,

\[
M = \frac{1}{N} \sum_i M_i e_i. \tag{7.1}
\]

Strictly speaking, the average magnetic moment should be calculated from the spin magnetic moments \( M_i \) (2.31) instead of the directions of the exchange-correlation field \( e_i \) (2.16), but we observed that the difference between the two quantities was small even for spin configurations far from the ground state – see section 12.3 for details. The energy and the magnetization were examined both for a fixed temperature as a function of time to describe switching events, and their time average as a function of temperature to quantify thermal equilibrium properties.

### 7.3 Layer simulations

For layered systems, we determined the interaction coefficients between the spins as discussed in section 2.6. The \( J_{ij}^{\alpha \beta} \) coefficients were calculated for neighbors within a circle of a given radius. The interactions are generally oscillating and decreasing slowly with distance, in agreement with the Ruderman–Kittel–Kasuya–Yosida theory\cite{[107–109]}. In most cases, we used a circle of radius of about 5-10 lattice constants, which was sufficient for the determination of the correct ground state and finite-temperature properties using the Hamiltonian (3.1). Unlike in the cluster model, the \( \tau \) matrices of layered systems are calculated in momentum space, so a sufficiently large number of \( k \) points is necessary for the precise determination of the interactions in real space. The effect of induced moments was not included in the calculations, since the adiabatic theory\cite{[47]} leading to the description by the Hamiltonian (3.1) only holds for stable moments.

At finite temperature, the system was examined by atomic spin dynamics and Monte Carlo simulations. The spin dynamics simulations followed the time evolution of the system through the numerical solution of the stochastic Landau–Lifshitz–Gilbert equation (5.6) as given in section 5.3. The Monte Carlo simulations relied on single-spin Metropolis dynamics\cite{[110]}: for a given spin \( S_i \), a random new direction \( S_i' \) is chosen uniformly on the unit sphere, and the spin is rotated into this direction with probability

\[
p_{\text{rotation}} = \min \left\{ 1, e^{-\frac{1}{k_B T} (H(S_i') - H(S_i))} \right\}. \tag{7.2}
\]
During a single Monte Carlo step, the algorithm went over all the spins in the lattice once.

Besides the temperature $T$, both spin dynamics and Monte Carlo simulations used the interaction parameters, the values of the magnetic moments and the external magnetic field as input parameters, along with the geometrical positions of the localized magnetic moments. The Gilbert damping $\alpha$ was a further parameter of spin dynamics simulations. Since spin dynamics simulates real time evolution, we also used a harmonically oscillating external field $B$ besides the static field during some calculations. In both simulation methods, we could set free or toroidal periodic boundary conditions.

Following the real-time or Monte Carlo dynamics of the spin vectors, we calculated several thermodynamic quantities. By substituting $S_i$ into (3.1), we could keep track of the energy of the system, which is especially important during Monte Carlo simulations since it determines the transition probabilities in (7.2). The energy determines the heat capacity of the system,

$$C = \frac{\langle E^2 \rangle - \langle E \rangle^2}{k_B T^2},$$

where $\langle \rangle$ denotes time or Monte Carlo ensemble averaging. We also calculated the Fourier transform of the spin vectors,

$$S_k = \frac{1}{N} \sum_i e^{-i k R_i} S_i,$$

which includes the magnetization $M = S_{k=0}$. Due to using a layered system, the Fourier transformation was only performed within two dimensions, and $S_k$ values for different layers were tracked separately. The static structure factor

$$S^{\alpha \alpha}(k) = \langle |S_{k}^{\alpha}|^2 \rangle,$$

$$S(k) = \sum_{\alpha} S^{\alpha \alpha}(k)$$

is connected to the elastic neutron scattering cross-section and determines the type of magnetic order in the system. For the exact connection between experimental scattering intensity and the Fourier transform of the spins the reader is referred to the handbook [111]. If $S(k)$ only takes a large finite value at $k = 0$, the spins are ordered ferromagnetically within the layer; peaks at finite $k$ values within the first Brillouin zone indicate noncollinear order, such as spin spirals with a single $k$ and hexagonal skyrmion lattices with triple $k$ vectors; while if (7.6) is small for all $k$ values, the system is paramagnetic. Note that $S(k)$ has a $k \leftrightarrow -k$ symmetry by definition.

For the calculation of the linear response, we required the variance of the Fourier transform of the spins,

$$\Delta S^{\alpha \alpha}(k) = \langle |S_{k}^{\alpha}|^2 \rangle - \langle S_{k}^{\alpha} \rangle^2,$$

$$\Delta S(k) = \sum_{\alpha} \Delta S^{\alpha \alpha}(k).$$

Expression (7.8) for $k = 0$ also leads to the static magnetic susceptibility,

$$\chi = \frac{N}{k_B T} \left( \langle M^2 \rangle - \langle M \rangle^2 \right) = \frac{N}{k_B T} \Delta S(k = 0).$$
Monte Carlo simulations generally required less computation time to determine the equilibrium properties of the system with the same precision. The advantage of spin dynamics simulations is the ability to follow the real time evolution of the system including transients, switching events such as skyrmion creation and annihilation, dynamical linear response and spin waves. For the characterization of the latter, we define the time-dependent lattice Fourier transform of the spin vectors similarly to (7.4),

\[ S_k(t) = \frac{1}{N} \sum_i e^{-ikR_i} S_i(t). \]  

(7.10)

Using (7.10), the dynamic structure factor[112] reads

\[ S^{\alpha \alpha}(k, \omega) = \int e^{i\omega t} \left( \langle S^\alpha_k(t) S^\alpha_{-k}(0) \rangle - \langle S^\alpha_k(t) \rangle \langle S^\alpha_{-k}(0) \rangle \right) dt, \]  

(7.11)

which is the simulative equivalent of the intensity obtained from inelastic neutron scattering experiments, analogously to its static counterpart (7.5)[111]. We emphasize that \( \langle \rangle \) in (7.11) denotes averaging over different realizations of the noise in the stochastic Landau–Lifshitz–Gilbert equation, since the simulation time is also used as a Fourier transformation variable. The different realizations correspond to initializing the random number generator with different seed values. The peaks in \( |S^{\alpha \alpha}(k, \omega)|^2 \) correspond to the excitations of the system with a given wave vector \( k \) and frequency \( \omega \), which can be identified with the spin waves discussed in chapter 3. We note that \( S^{\alpha \alpha}(k, \omega) \) is only determined for certain discrete \( k \) and \( \omega \) values during the simulation. The lattice constants determine the size of the Brillouin zone, while the size of the simulated lattice sets the distance between the allowed \( k \) points; for the time parameter, the time between measurements of (7.10) and the total simulation time play an analogous role. The finite lattice size also determines the wave vectors of spin spirals and the periodicity of skyrmion lattices allowed during the simulations; for a detailed discussion see appendix B.6.
Chapter 8

Spin wave spectrum of a ferromagnetic monolayer

Ultrathin Fe films on W(110) substrate have represented a standard system for investigating magnetism in reduced dimensions since the 1980s[113]. Although the experiments have to be performed in ultra-high vacuum, the good thermal stability[114] of the samples makes it possible to create the islands and layers of Fe in different geometries[115, 116]. Using scanning tunnelling microscopy[115], an in-plane ferromagnetic spin configuration was identified in the magnetic layer, with the critical temperature depending on the Fe coverage, being $T_c \approx 230$ K for the monolayer and $T_c \approx 450$ K for the double-layer.

Besides the ground state properties, the excitations of the systems have also been in the focus of previous research. In thin films, the magnetic dipolar interaction and the reduced dimensionality lead to the appearance of spin wave modes which are absent in bulk systems[61, 62, 117]. The effect of the dipolar interaction on the ferromagnetic resonance lineshape has been thoroughly discussed both in theoretical[118–120] and in experimental[121–124] studies.

The spin wave spectrum of ultrathin ferromagnets differs from the bulk case not only due to demagnetizing effects. The breaking of inversion symmetry of the bulk system leads to the appearance of the Dzyaloshinsky–Moriya interaction[12, 13]. It has been predicted theoretically in [14] that in an Fe monolayer on W(110), where the magnetization is along the [110] direction, the Dzyaloshinsky–Moriya interaction leads to the asymmetry of the spectrum for spin waves with wave vectors parallel to the [001] direction; that is, perpendicular to the magnetization. Although a similar asymmetry has already been demonstrated in bulk Cs$_2$CuCl$_4$[125], future applications of the effect are more promising in nanostructures created from ultrathin films, where the spin wave spectrum can be fine-tuned[126].

Inelastic neutron scattering is an appropriate method for experimentally determining the spin wave frequencies, but it can mainly be used in bulk systems where the large number of excitations compensates for the generally low scattering cross-section. In ultrathin films, spin-polarized electron energy loss spectroscopy has been successfully applied for the same purpose[127]; the fact that electrons can only probe the surface layers of a metal due to Coulomb repulsion is actually an advantage in this scenario. Unlike ferromagnetic resonance experiments, the method is also applicable for excitations with higher wave vectors. Using this technique, the asymmetry of the spin wave spectrum in Fe double-layer on W(110) has also been proven experimentally in [15, 16] – see figure 8.1(a).

In this chapter, we will demonstrate how the spin wave frequencies discussed in chap-
Figure 8.1: Spin wave spectrum in Fe ultrathin films on W(110), measured using spin-polarized electron energy loss spectroscopy. Panel (a) from [16]: spin wave frequencies as a function of wave vector in the double-layer. Due to the Dzyaloshinsky–Moriya interaction, the spectrum is asymmetric with respect to switching the magnetization direction or flipping the sign of the wave vector. Panel (b) from [17]: softening of the spin wave frequencies at elevated temperature in the monolayer.

Chapter 3 can be determined from atomistic spin dynamics simulations introduced in section 7.3. We will use a model Hamiltonian of the form (3.1) which can qualitatively reproduce the ground state and spin wave spectrum of an Fe monolayer on W(110) surface. The spin wave frequencies will be obtained by determining the linear response of the spin system similarly to a resonance experiment, which in a simulation can also be performed for excitations with finite wave vectors; and by calculating the amplitude of thermally excited spin waves.

There exist several experimental[17] as well as simulational[18] investigations for Fe monolayer on W(110) displaying the decrease of spin wave frequencies with increasing temperature – see figure 8.1(b). However, the theoretical description is generally lacking in the literature. We will demonstrate that the simple theories developed for spin waves in bulk systems, which are summarized in chapter 4, are able to quantitatively reproduce the temperature dependence of spin wave frequencies obtained from the simulations.

The focus of the present chapter is the demonstration of the simulation methods; the results of *ab initio* calculations for Fe monolayer on W(110) will only be presented in chapter 9.

### 8.1 Spin wave spectrum and linear response

The monolayer is illustrated in figure 8.2. In the global coordinate system, the $z$ axis is pointing outwards from the surface along the [110] direction, while the in-plane $x$ and $y$ axes are parallel to the [110] and [001] directions, respectively. It is known from experiments and *ab initio* calculations that the system is ordered ferromagnetically along the $x$ axis. Therefore, we considered ferromagnetic scalar Heisenberg coupling between the nearest neighbours $J^{xx} = J^{yy} = J^{zz} = J < 0$. The on-site anisotropy matrix is diagonal due to the $C_{2v}$ symmetry of the system; we only included $K^{zz} < 0$ in the Hamiltonian and set $K^{yy} = K^{zz} = 0$, which determined the easy axis. We also considered the Dzyaloshinsky–Moriya interaction $D$ between the next-nearest neighbours, since the
Figure 8.2: Sketch of the (110) surface of a bcc lattice. The \( x, y \) and \( z \) axes correspond to the [110], [001] and [110] crystallographic directions, respectively. The nearest-neighbour scalar Heisenberg exchange \( J \) and next-nearest-neighbour Dzyaloshinsky–Moriya \( D \) interactions are denoted at the atomic positions the central atom 0 interacts with. The easy axis \( K^{zx} < 0 \) is along the \( x \) axis.

\textit{ab initio} calculations indicated that this type of interaction is the strongest between these pairs of atoms – see section 9.1. The magnitude of \( D \) was chosen such that the ground state remained ferromagnetic, while its direction is in agreement with symmetry considerations and \textit{ab initio} calculations.

The spin wave spectrum of the system was already calculated in section 6.2. Substituting the lattice-specific Fourier transforms of the interactions into (6.5) yields

\[
\omega_k = \frac{\gamma}{M} \left( -4J \left[ 1 - \cos \left( \frac{\sqrt{2}}{2} ak^x \right) \cos \left( \frac{1}{2} ak^y \right) \right] \right) - 2D \sin (ak^y) - 2K^{zx}. \tag{8.1}
\]

The sign of the Dzyaloshinsky–Moriya interaction \( D \) is positive if the vector is pointing in the direction specified in figure 8.2. The spin wave spectrum along the \( k^y \) axis is sketched in figure 8.3. It can be seen that the spectrum is asymmetric with respect to the \( \Gamma \) point in the Brillouin zone due to the Dzyaloshinsky–Moriya interaction. Equation (8.1) indicates that the Dzyaloshinsky–Moriya interaction only influences the spectrum along the \( k^y \) axis, that is, the direction perpendicular to the Dzyaloshinsky–Moriya vector. The minimum of the spectrum is shifted towards finite wave vectors. The ferromagnetic ground state is stable as long as all the spin wave frequencies \( \omega_k \) are nonnegative, which corresponds to the stability condition discussed in detail in section 6.2. This means that the Dzyaloshinsky–Moriya interaction tries to destabilize the ferromagnetic state, since it prefers a noncollinear spin configuration, but the on-site \( K^{zx} \) anisotropy keeps the system in the ground state by inducing a gap in the spin wave spectrum.

One way to determine the excitation frequencies of the system during the simulations is measuring the linear response to an external perturbing magnetic field. This forms the
basis of magnetic resonance experiments. In the simulations, we will use a perturbation of the form $B_i^z \cos(\Omega t)$, and measure the response of the system as a function of $\Omega$. We note that in resonance experiments it is generally complicated to alter the frequency of the perturbing field, and instead the spin wave frequencies are modified by applying a magnetic field parallel to the ferromagnetic direction; this difficulty does not arise during spin dynamics simulations. We also suppose that the perturbing field may be inhomogeneous on the atomic scale, while it is homogeneous in actual resonance experiments, meaning that there is no momentum transfer. In the simulations the inhomogeneous field can be used to measure the spin wave frequencies at finite wave vectors; under experimental conditions, this necessitates using a different method such as inelastic neutron or electron scattering.

The linear response of the system in the simulations will be characterized by the variance of the Fourier transform of the spins defined in (7.7),

$$\Delta S^\perp (k) = \Delta S^{yy} (k) + \Delta S^{zz} (k).$$  \hfill (8.2)

The explicit form of (8.2) can be calculated analytically by linearising the Landau–Lifshitz–Gilbert equation (5.4). If we consider an external perturbation of the form $B_i^z = B^z \cos (kR_i)$, meaning that it corresponds to a single harmonic standing wave, then the linear response function reads

$$\Delta S^\perp (k) = \frac{|\gamma B_k^z|^2}{8(1 + \alpha^2)} \left\{ \left[ \left( \frac{\Omega + \omega_k}{1 + \alpha^2} \right)^2 + \left( \frac{\alpha \omega_k}{1 + \alpha^2} \right)^2 \right]^{-1} \right. \left[ \left( \frac{\Omega - \omega_k}{1 + \alpha^2} \right)^2 + \left( \frac{\alpha \omega_k}{1 + \alpha^2} \right)^2 \right]^{-1} \right. \left[ \left( \frac{\Omega + \omega_{-k}}{1 + \alpha^2} \right)^2 + \left( \frac{\alpha \omega_{-k}}{1 + \alpha^2} \right)^2 \right]^{-1} \right. \left[ \left( \frac{\Omega - \omega_{-k}}{1 + \alpha^2} \right)^2 + \left( \frac{\alpha \omega_{-k}}{1 + \alpha^2} \right)^2 \right]^{-1} \right\}.$$  \hfill (8.3)

![Figure 8.3: Spin wave spectrum of the system with model parameters $J = -1$, $D = 0.1$ and $K^{zz} = -0.1$. Compare with the experimental results in figure 8.1(a).](image-url)
with \( B_{k}^{z} = \frac{1}{N} \sum_{i} e^{-ikR_{i}} B_{i}^{z} \).

The expression (8.3) indicates that the perturbing field excites the system at \( k \) and \(-k\) wave vectors, and the response of the system is enhanced if the excitation frequency \( \Omega \) is in resonance with the spin wave frequencies of the system \( \omega_{k}, \omega_{-k} \). There are at least two peaks in \( \Delta S^{\perp}(k) \) at \( \Omega = \pm \omega_{k} \), which are simply a consequence of the form of the excitation \( \cos(\Omega t) \). However, the difference between \( \omega_{k} \) and \( \omega_{-k} \), which again doubles the number of peaks, is caused by the Dzyaloshinsky–Moriya interaction, and therefore gives information about the interactions in the system. The Gilbert damping \( \alpha \) is responsible for the finite linewidth of the peaks in (8.3), and it also slightly influences the resonance frequencies.

### 8.2 Temperature effects on the spectrum from perturbation theory

We will include temperature effects in the calculations by following the perturbative treatment of the Hamiltonian (3.1) discussed in section 4.1. For the model Hamiltonian considered in this chapter, with the ferromagnetic ground state along the \( x \) direction, Dzyaloshinsky–Moriya interaction and on-site anisotropy terms, the first-order perturbative correction to the free energy in (4.9) may be expressed in a closed form. The expectation value of the quartic term \( H_{1} \) in (4.8) reads

\[
\langle H_{1} \rangle_{\text{SW}} = 2J \frac{1}{N} \sum_{k,k'} \left( 1 + \gamma_{k-k'}^{(1)} - 2\gamma_{k'}^{(1)} \right) \frac{\gamma}{M} n_{k} \frac{\gamma}{M} n_{k'}
+ 2K^{xx} \frac{1}{N} \sum_{k,k'} \frac{\gamma}{M} n_{k} \frac{\gamma}{M} n_{k'} + 2D \frac{1}{N} \sum_{k,k'} \gamma_{k'}^{(2)} \frac{\gamma}{M} n_{k} \frac{\gamma}{M} n_{k'},
\]

where \( \gamma_{k}^{(1)} = \cos \left( \frac{\sqrt{2}}{2} ak^{x} \right) \cos \left( \frac{1}{2} ak^{y} \right) \) and \( \gamma_{k}^{(2)} = \sin \left( ak^{y} \right) \) are geometrical factors characterizing the lattice. After minimization of the free energy, this leads to the finite-temperature spin wave frequencies

\[
\omega_{k}(T) = \frac{\gamma}{M} \left[ -4J \left( 1 - \gamma_{k}^{(1)} \right) - 2K^{xx} - 2D \gamma_{k}^{(2)} 
+ 4J \frac{1}{N} \sum_{k'} \left( 1 + \gamma_{k-k'}^{(1)} - \gamma_{k'}^{(1)} - \gamma_{k}^{(1)} \right) \frac{\gamma}{M} n_{k'}
+ 4K^{xx} \frac{1}{N} \sum_{k'} \frac{\gamma}{M} n_{k'} + 2D \frac{1}{N} \sum_{k'} \left( \gamma_{k'}^{(2)} + \gamma_{k}^{(2)} \right) \frac{\gamma}{M} n_{k'} \right].
\]

Since all corrections to the zero-temperature value appear with an opposite sign in (8.5), it is straightforward to see that the spin wave frequencies will decrease at finite temperature.

We note that there are some limitations to applying the method described in section 4.1 to the linear response of the classical spin system. Since the perturbative method is not based on the Landau–Lifshitz–Gilbert equation, it obviously cannot describe corrections due to the presence of the Gilbert damping \( \alpha \) as was shown in (8.3). Fortunately, these corrections are generally small in the limit \( \alpha \ll 1 \), which usually holds for most ferromagnetic materials and in our simulations. The perturbation method cannot calculate
the finite linewidth of the response function, either, since the broadening is another consequence of the damping. Keeping these limitations in mind, the results of the calculations will be compared to numerical simulations in section 8.4.

8.3 Simulation results at zero temperature

We performed spin dynamics simulations on the model system discussed in section 8.1. The simulations were started from a ferromagnetic configuration along the $x$ axis at zero temperature, and a time-dependent external magnetic field $B^x(t) = B^x \cos (\Omega t) \cos \left( k R_i \right)$ was applied. The response of the system was calculated from the Fourier transform of the transversal components of the spins, $\Delta S^\perp$ defined in (8.2). By changing the excitation frequency $\Omega$, we obtained resonance curves comparable to the prediction of linear response theory given by (8.3).

Figure 8.4 demonstrates the agreement between theory and simulations. At finite wave vector $k^y = 0.0625$, the resonance peak is shifted to higher frequencies. If the Dzyaloshinsky–Moriya interaction is also present in the system, the resonance peak splits into two distinct peaks, corresponding to the different frequencies of spin waves with wave vectors $k$ and $-k$.

Another way of determining the spin wave frequencies of the system is based on the calculation of the dynamic structure factor $S^{\alpha \alpha}(k, \omega)$ defined in (7.11). Similarly to the linear response scenario, the wave-vector-excitation frequency pairs may be determined from the transversal component of the spins,

$$S^\perp(k, \omega) = |S^{yy}(k, \omega)|^2 + |S^{zz}(k, \omega)|^2. \quad (8.6)$$

In this case, the presence of an external magnetic field is unnecessary, the frequency parameter appears due to performing Fourier transformation in time. However, some sort of excitation is required for the creation of spin waves in the system; therefore, we performed the calculations at finite temperature. Since it was found in section 8.2 that the spin wave frequencies depend on the temperature, $T$ must be sufficiently low to approximate the zero-temperature spin wave frequencies. For the parameters $J = -1, D = 0.1, K^{xx} = -0.1$ in the model Hamiltonian, we found that $k_B T = 0.01$ is appropriate for the simulations, being significantly lower than the Curie temperature $k_B T_c \approx 0.7$.

Figure 8.5 shows that the peaks of $S^\perp(k, \omega)$ correspond to the spin wave frequencies (8.1). The frequencies should increase monotonically at high wave vectors, but due to the finite resolution in time $1 M/\gamma$, they are mirrored back below $\pi \gamma / M$. Although the dynamic structure factor gives information about the whole spectrum during a single run, the results are generally more noisy than in the case where a spin wave with a specific wave vector is amplified by the external excitation. Therefore, we determined the spin wave frequencies at higher temperature from the linear response method.

8.4 Temperature dependence of the spin wave energies

At finite temperature, we fitted a function of the form (8.3) to the simulation results, and identified the locations of the resonance peaks with the spin wave frequencies of the system. These frequency values were compared to the spectrum calculated from perturbation theory (8.5). At zero temperature, both methods simplify to the theoretical spin
Figure 8.4: Linear response function of the system $\Delta S^\perp (k)$ as a function of the frequency of the excitation $\Omega$ (a) from theory (8.3) and (b) from simulations; the peaks are indicated by arrows. The Dzyaloshinsky–Moriya parameter is $D = 0.0$ in the first two curves and $D = 0.1$ in the last one; the wave vector of the excitation is $k^y = 0.000000 \frac{2\pi}{a}$ in the first case and $k^y = 0.062500 \frac{2\pi}{a}$ in the other two. The further simulation parameters were set to the values $J = -1, K^{xx} = -0.1, \alpha = 0.05, B^z = 0.004, k_BT = 0$ and $N = 32 \times 32$. The averaging was performed over a simulation length of 10000 $M/\gamma$ after waiting 5000 $M/\gamma$ for the transients to decay, with the time step $\Delta t = 0.01 M/\gamma$. 
Figure 8.5: The dynamic structure factor $S^\perp (k, \omega)$ as a function of $k^y$ and $\omega$, for $k^x = 0$. The simulation parameters are $J = -1, D = 0.1, K^{xx} = -0.1, \alpha = 0.05, k_B T = 0.01$ and $N = 32 \times 32$. The zero-temperature spin wave spectrum (8.1) is shown by open circles. The black line is a guide to the eye; due to the finite lattice size, $S^\perp (k, \omega)$ is only determined for fixed wave vectors. After thermalizing the system for $3000 \, M/\gamma$, the Fourier transformation was performed over a simulation length of $1000 \, M/\gamma$, and averaged over 100 realizations. The time resolution of the Fourier transformation was $1 \, M/\gamma$, which constrained the observable spin wave frequencies between 0 and $\pi \, \gamma/M$; higher values appear mirrored back to lower frequencies.

wave spectrum (8.1), apart from corrections of the order $\alpha^2$. For the model parameters used throughout this chapter, the Curie temperature of the system is $k_B T_C \approx 0.7$, and since the theoretical method is constructed by starting from the ferromagnetic state, we can only expect an agreement between theory and simulations well below this temperature.

Figure 8.6 shows that the perturbation theory in section 8.2 correctly predicts the softening of the spin wave frequencies at finite temperature. Although the fact that the theoretical description does not account for the Gilbert damping $\alpha$, which parameter influences the locations of the peaks, there is a good quantitative agreement between theory and simulations over the whole considered temperature range.

It can be seen in figure 8.7 that the spin wave softening is more pronounced at higher wave vectors, indicating that the curvature of the spectrum also decreases with increasing temperature – see [59] for a more detailed investigation of this effect. Theory and simulation are once again in good quantitative agreement for all considered wave vectors. This means that the perturbative method provides a sufficient description of the experimentally observed softening of the spin wave frequencies shown in figure 8.1(b).
Figure 8.6: Comparison of theory and simulations for the temperature dependence of the frequency of the spin wave with wave vector $k^x = 0, k^y = 0.0625002\pi$. The model parameters are $J = -1, D = 0, K^{xx} = -0.1, \alpha = 0.05$ and $N = 32 \times 32$. The averaging was performed over a simulation length of $5000 M/\gamma$ after a thermalization of $5000 M/\gamma$, with the time step $\Delta t = 0.01 M/\gamma$.

Figure 8.7: The temperature dependence of the spin wave spectrum with Dzyaloshinsky–Moriya interaction, for $k^x = 0$. The model parameters are $J = -1, D = 0.1, K^{xx} = -0.1, \alpha = 0.05$ and $N = 32 \times 32$. The averaging was performed over a simulation length of $5000 M/\gamma$ after a thermalization of $5000 M/\gamma$, with the time step $\Delta t = 0.01 M/\gamma$. Compare with the experimental results in figure 8.1.
Chapter 9

Fe mono- and double-layer on W(110): spin reorientation transitions

Besides its experimentally determined spin wave spectrum discussed in the previous chapter, double-layer Fe on W(110) is also notable for motivating research in non-collinear spin configurations in two-dimensional systems. Spin-polarized scanning tunnelling microscopy[128] provides an experimental way for determining the magnetic structure with atomic resolution, by taking advantage of the spin-dependent density of states of magnetic tips. It was demonstrated using this method[129] that at low temperature, the magnetic pattern corresponds to periodically arranged stripe domains, with domain walls along the [1\overline{1}0] direction. One crucial difference to the high-temperature case is that the magnetization in the domains points out-of-plane along the [110] axis, instead of the in-plane [1\overline{1}0] direction. The periodic nature of the magnetization motivated further investigations, and it was demonstrated in [19] that the ground state of the system corresponds to a spin spiral state with a wavelength of \lambda \approx 40\,\text{nm}. The spin spiral is shown in figures 9.1(a)-(b); the spins are rotating in the [001]-[110] plane, which is perpendicular to the magnetic easy axis observed at high temperature in the double-layer and down to low temperature in the monolayer – see chapter 8. The spin spiral state is created due to the Dzyaloshinsky–Moriya interaction in the system, but the anisotropy is sufficiently strong to distort the spiral such a way that it resembles a sequence of out-of-plane ferromagnetic domains with narrow in-plane magnetized domain walls between them.

\textit{Ab initio} calculations in [106] have predicted the rotational sense of the spin spiral owing to the Dzyaloshinsky–Moriya interaction, even before the experimental verification in [19]. However, the calculations[88, 106] could not reproduce the spin spiral state as the energy minimum of the system at zero temperature, although they confirmed the out-of-plane [110] direction of the easy axis. In this description, the domain walls between the ferromagnetic areas are energetically unfavourable, while in the spin spiral the rotation of the spins minimizes the energy of the system.

A further question concerns the direction of the easy axis in the system as a function of temperature. It was demonstrated in [20] that the stripe structure disappears from the system around 200\,\text{K}, shown in figures 9.1(c)-(d). This establishes the connection between the low-temperature spin spiral phase and the high-temperature ferromagnetic phase with the magnetization perpendicular to the spiral plane. The disappearance of the spin spiral phase is necessary for the observation of the chiral asymmetry in the spin wave spectrum discussed in chapter 8; the asymmetry must disappear for spin waves measured in a spin spiral or an out-of-plane ferromagnetic state[89, 90]. Finally, we note that the
Figure 9.1: Spin-polarized scanning tunnelling microscopy measurements performed on Fe double-layer on W(110) surface. Panels (a) and (b) from [19]: right-rotating cycloidal spin spiral ground state observed at $T = 4.7$ K in the double-layer areas of 1.7 Fe atomic layers. All components of the spin were measured by rotating the magnetization of the tip by external magnetic field. Panels (c) and (d) from [20]: disappearance of the spiral modulation at elevated temperature in the double-layer areas of 1.6 Fe atomic layers. The reorientation temperature depends on the coverage of the second Fe layer, reaching 200 K for 2.0 atomic layers. It was only possible to measure the out-of-plane component of the spins with the nonmagnetic tip.

reorientation temperature of the easy axis strongly depends on the size and shape of the double-layer areas in the experiments[20, 130].

In this chapter, we present the results of ab initio calculations for Fe mono- and double-layers on W[110] surface following the methodology discussed in sections 7.1 and 7.3. The ferromagnetic ordering in the monolayer is in agreement with the experiments; for the double-layer, we find an out-of-plane ferromagnetic ground state[88, 106] instead of the spin spiral state[19], but the reorientation of the easy axis at higher temperature can be sufficiently explained. We will also demonstrate using a model Hamiltonian that the experimentally observed transition from the spin spiral phase at low temperature to the ferromagnetic state perpendicular to it can be reproduced in Monte Carlo simulations and explained within mean-field theory from section 4.3. We also predict the presence of an elliptic conical spin spiral state between the planar spiral and ferromagnetic phases.

9.1 Calculated exchange interactions and ground states

The details of the ab initio calculations are summarized in appendix D.1. Since Fe has a significantly smaller lattice constant than W ($a_{Fe} = 2.867$ Å and $a_{W} = 3.165$ Å in bcc structure), it is expected that the perfect bulk geometry becomes distorted around the Fe layers. This is amplified by common relaxation effects at the surface due to the reduced coordination number of atoms. In the calculations, we modelled this by a reduced distance between the topmost W layer and the Fe layer as illustrated in figure 9.2, and also between the Fe layers in the double-layer scenario. In the following, this distance will be given by the inward relaxation of the layers in percentage of the ideal W-W layer distance in the [110] direction. For the Fe monolayer, theoretical calculations using the linearised augmented plane wave method obtained relaxation values between 12%-13%[18, 131–133], while experimentally determined values fall in the range of 7%-13%[134–136]. For the double-layer, the relaxation values were calculated from ab initio methods in [93], yielding 10% between the topmost W layer and the neighbouring Fe layer, and 23.5%
Figure 9.2: Sketch of Fe monolayer on W(110) surface. Due to the smaller size of the Fe atoms, the $d_{\text{Fe-W}}$ distance is decreased with respect to the $d_{\text{W-W}}$ distance in the ideal lattice by the relaxation $r_{\text{Fe-W}}$.

between the Fe layers.

Since the relaxation values found in the literature depend on the applied theoretical or experimental method, we performed the $ab\ ini\io$ calculations for different geometries to test the stability of the ground state and the parameters in the model Hamiltonian (3.1). For the monolayer, we used relaxation values between 10% and 17%. For the double-layer, we changed the Fe-W relaxation between 8% and 15%, while the Fe-Fe distance was kept fixed at 23.5% relaxation. The Wigner–Seitz radius of the Fe atoms was modified according to the total volume of the layered system. All the other layers were kept in the ideal geometry; previous calculations[131–133] indicate that the W-W layer distances relax by less than 1%, and therefore can be considered negligible.

Figure 9.3 displays the calculated exchange interactions appearing in the Hamiltonian (3.1) for the monolayer. The nearest-neighbour ferromagnetic coupling is fairly insensitive to the relaxation, while the next-nearest-neighbour coupling at the distance of one lattice constant is antiferromagnetic for lower relaxations, but becomes ferromagnetic above 15% relaxation. The in-plane components of the Dzyaloshinsky–Moriya vectors are shown in figures 9.3(b)–(c), where the $x$ and $y$ directions correspond to the $[\bar{1}T0]$ axis and to the $[001]$ axis as in chapter 8. They are comparable in magnitude to the scalar Heisenberg exchange interactions, and they also show oscillating behaviour with the distance. With our sign convention and only taking into account the largest Dzyaloshinsky–Moriya interactions in both directions, the $D_{ij}^x$ component prefers a right-rotating spiral along the $[001]$ direction and the $D_{ij}^y$ component prefers a left-rotating spiral along the $[\bar{1}T0]$ direction – see the definitions in section 6.1. This is in agreement with earlier theoretical calculations[88, 106]. As will be shown below, the ground state of the system remains ferromagnetic, so the Dzyaloshinsky–Moriya interactions only influence the chirality of Néel domain walls instead of the chirality of spirals.
Figure 9.3: Calculated (a) scalar Heisenberg exchange interactions (2.39) and (b)-(c) Dzyaloshinsky–Moriya vector components (2.37) for Fe monolayer on W(110) surface, for different relaxation values. For the Dzyaloshinsky–Moriya vectors, displayed are the values for the pairs with \( R_{ij}^x > 0 \) and \( R_{ij}^y > 0 \), while for the rest of the pairs they may be obtained from the symmetry relations described in appendix D.2. Multiple data points at the same distance denote neighbours not connected by symmetry.

Figure 9.4: Calculated (a) scalar Heisenberg exchange interactions (2.39) and (b)-(d) Dzyaloshinsky–Moriya vector components (2.37) for Fe double-layer on W(110) surface, for 10% relaxation of the Fe layer next to the substrate. The 1 and 2 numbers denote the outer and inner Fe layers, respectively. For the Dzyaloshinsky–Moriya vectors, displayed are the values for the pairs with \( R_{ij}^x > 0 \) and \( R_{ij}^y > 0 \), while for the rest of the pairs they may be obtained from the symmetry relations described in appendix D.2. Multiple data points at the same distance denote neighbours not connected by symmetry.
Figure 9.5: Phase diagram of Fe monolayer on W(110) substrate. Shown are the energies per spin of ferromagnetic (FM) orientations along different crystallographic directions, displaying the reorientation of the easy axis from the in-plane [1T0] to the out-of-plane [110] direction by increasing relaxation.

The exchange interactions for the double-layer are summarized in figure 9.4. Since there are more coupling coefficients due to the increased number of layers, they are only illustrated for 10% relaxation of the Fe-W distance. Similarly to the monolayer, the scalar Heisenberg exchange interactions are strongly ferromagnetic at short distances. Regarding the chirality of the cycloidal spin spirals and Néel domain walls, it can be seen that the strongest $D_i^y$ components have changed sign with respect to the monolayer, while the $D_i^y$ components have not, leading to a left-rotating spin spiral along both the [001] and [1T0] directions. Unfortunately, the rotational sense along the [001] direction is in contradiction with previous theoretical [88, 106] and experimental [15, 19] results. The rotational sense remains the same as the Fe-W distance is modified. This indicates that our ab initio results cannot perfectly reproduce the experimentally observed behaviour of Fe double-layer on W(110).

We determined the ground state of the system by performing zero-temperature spin dynamics simulations and approximating the energies of the spin spiral states from the Fourier transform of the exchange tensors – see (B.69) in appendix B.5. The results are summarized in figure 9.5. Although the ground state energy of the magnetic system changes as the exchange coupling coefficients are modified due to the relaxation, the only qualitative difference is that the easy axis of the monolayer is reoriented from the in-plane [1T0] to the out-of-plane [110] direction around 15% relaxation value, while the system remains ferromagnetic for all relaxations. The in-plane easy axis at the experimentally observed relaxation value of 13% is in agreement with the experiments [137]. The Dzyaloshinsky–Moriya vectors are not strong enough to create a spin spiral ground state in the system. Theoretically a spin spiral state should be the ground state at the transition point where the [1T0] and [110] directions are degenerate for an arbitrarily weak Dzyaloshinsky–Moriya vector component along the [001] axis – see the continuum
approximation for the creation of spin spiral ground states in section 6.3, equation (6.13) for $\tilde{K} = 0$. However, this occurs in a very narrow relaxation interval (< 0.1%) which could not be resolved by the ab initio calculations.

The ground state of the double-layer is out-of-plane ferromagnetic at all considered relaxation values. This is in agreement with earlier theoretical calculations [88, 106]. As was discussed in the introduction of the chapter, the direction of the easy axis agrees with the experiments [130], but the ground state should correspond to a spin spiral state with $\lambda \approx 40\text{nm}[19]$, see figure 9.1. We have confirmed that in our simulations, spin spiral states with wavelengths up to 40 nm are metastable with respect to the ferromagnetic state, while the micromagnetic model applied in [88, 106] rules out the presence of a spin spiral ground state with any wavelength, as the Dzyaloshinsky–Moriya interaction is below the critical value (6.13). In [19], the creation of the spin spiral state was explained by the presence of the magnetostatic dipolar interaction; we have checked that including this interaction does not create a spin spiral state, but reorients the easy axis towards the in-plane [110] direction at lower relaxation values. In conclusion, ab initio methods probably cannot determine the parameters in the model Hamiltonian with the precision required for the distinction between a ferromagnetic state and such a strongly distorted spin spiral state with a very long wavelength; this is in part explained by the numerical difficulties (e.g. the numerical integration in the Brillouin zone), and in part due to the systematic errors in the approximations used.

9.2 Finite-temperature phase transitions

Using the coupling coefficients determined from ab initio calculations, we performed Monte Carlo simulations to identify possible phase transitions in the system as a function of temperature. The phases were characterized by the static structure factor $S^{aa}(k)$ (7.5). Following the notations of chapter 8, we have identified the [110], [001] and [111] crystallographic directions with the $x, y$ and $z$ axes, respectively.

For the monolayer, such phase transitions are expected close to 15% relaxation, where the reorientation occurs due to changes in the geometry – see figure 9.5. Close to this point, the two-site anisotropy favours the $z$ axis, while the on-site anisotropy prefers the $x$ direction. In this case, mean-field theory suggests the possibility of a reorientation transition from the in-plane $x$ towards the out-of-plane $z$ direction as the temperature is increased. Note that the role of the $x$ and $z$ axes is interchanged compared to section 4.3. At exactly 15% relaxation, we have observed no reorientation transition in the Monte Carlo simulations shown in figure 9.6. This means that the reorientation only happens for smaller initial anisotropy at slightly higher relaxation, for which we have not performed ab initio calculations – at 15.1% relaxation, the ground state is already out-of-plane ferromagnetic. Reassuringly, such temperature-dependent reorientation transitions were not observed in the experiments, either [115]. The obtained critical temperature $T_C \approx 350\text{K}$ is somewhat higher than in the experiments, $T_C \approx 230\text{K}$.

For the double-layer, we considered 10% relaxation [93] between the top W and the neighbouring Fe layer, as no reorientation transition happened as a function of the distance at zero temperature. We explicitly added the magnetostatic dipolar interaction (2.41) to the calculated coupling coefficients. This term is not included in the ab initio calculations, but it is generally significantly smaller than the exchange interactions, and can usually be ignored in ultrathin film systems with characteristic spin patterns.
Figure 9.6: Static structure factor $S^{\alpha\alpha}(k)$, describing the magnetization components, as a function of temperature $T$. The results are obtained from Monte Carlo simulations for Fe monolayer on W(110) at 15% relaxation, for lattice size $N = 64 \times 64$. The averaging was performed over a simulation length of $10^6$ steps after a thermalization of $2 \times 10^5$ steps.

Figure 9.7: Static structure factor $S^{\alpha\alpha}(k)$, describing the magnetization components, as a function of temperature $T$. The results are obtained from Monte Carlo simulations for Fe double-layer on W(110) at 10% relaxation of the Fe-W distance, for lattice size $N = 32 \times 256 \times 2$. The 1 and 2 indices label the different layers as in figure 9.4. The averaging was performed over a simulation length of $10^6$ steps after a thermalization of $10^5$ steps.
on the nanometre scale. The change in the coupling coefficients when the geometry is
modified is of the same order of magnitude as the dipolar interaction; for example, using
the exchange interactions calculated for 8% instead of 10% relaxation and omitting the
dipolar term leads to comparable results. Contrary to the monolayer, here the out-of-
plane direction is preferred by the on-site anisotropy, while the two-site terms prefer an
in-plane orientation of the spins, coinciding with the case discussed in section 4.3. The
Monte Carlo simulations shown in figure 9.7 indicate a continuous reorientation transition
around \( T_r \approx 300 \text{ K} \) below the Curie temperature at \( T_C \approx 450 \text{ K} \). Although we have only
considered a single anisotropy parameter in the mean-field model in section 4.3 where the transition is instantaneous, different anisotropy parameters in the two Fe layers may
turn the transition continuous even in the mean-field description[81]. It can also be seen
in figure 9.7 that \( S^{xx}(k = 0) \) and \( S^{zz}(k = 0) \) are slightly larger in the second Fe layer,
probably due to the stronger ferromagnetic exchange interactions – see figure 9.4(a).

The obtained Curie temperature is in good agreement with the value \( T_C \approx 450 \text{ K} \) de-
termined experimentally in [115]. As shown in figures 9.1(c)-(d)[20], the spin spiral state
disappears from the system in experiments at higher temperature; the perfect double-
layer becomes in-plane ferromagnetic at around \( T_r \approx 200 \text{ K} \). Although our simulations
cannot reproduce the presence of a spin spiral state even at finite temperature and by
using an elongated simulation cell \( N = 32 \times 256 \times 2 \) along the experimental spin spiral
wave vector direction [001], the obtained reorientation temperature is in relatively good
agreement with the experiments. The reorientation temperature may depend on further
parameters: in the simulations with the coupling coefficients for 8% relaxation, it becomes
somewhat lower; in the experiments, the out-of-plane magnetization in the layer further
away from the substrate may persist up to room temperature in some geometries[130].
Finally, we mention that earlier theoretical descriptions[88, 106, 138] used a micromag-
netic model with a single anisotropy parameter, which model cannot account for a spin
reorientation transition at finite temperature.

9.3 Spin reorientation transition from the ferromag-
netic state to the spin spiral state in the perpen-
dicular plane

Although we have not observed a reorientation of the easy axis with the \( ab \ initio \)
exchange interactions in Fe monolayer on W(110), such a phase transition is possible in
the case of a model Hamiltonian. We will use the same system as in chapter 8, shown
in figure 9.8, which includes isotropic ferromagnetic exchange interaction \( J < 0 \) between
the nearest neighbours, Dzyaloshinsky-Moriya interaction \( D_{ij} = (D_{ij}, 0, 0) \) between the
next-nearest neighbours, and easy-axis on-site anisotropy \( K^{xx} < 0 \). The direction of the
Dzyaloshinsky-Moriya vectors is in agreement with the results of the \( ab \ initio \) calculations
depicted in figure 9.3(b).

For the calculations and the simulations we used the model parameters \( J = -1, D = 0.349 \) and \( K^{xx} = -0.12 \); the ground state is ferromagnetic along the \( x \) axis in this
case, but the gap is significantly smaller than in the calculations discussed in chapter 8
and shown in figure 8.3. It is known from the spin wave analysis in section 6.2 that the
spin spiral state cannot be stable with the same coupling coefficients. However, it
was shown in section 8.4 that the spin wave energies, and therefore the gap in the spec-
Figure 9.8: Sketch of a monolayer on the (110) surface of a bcc lattice. The $x$, $y$ and $z$ axes correspond to the [110], [001], and [110] crystallographic directions, respectively. The central atom $0$ interacts with the nearest neighbours by scalar Heisenberg exchange couplings $J$ and with the next-nearest neighbours by Dzyaloshinsky–Moriya vectors $D$ denoted by arrows. The easy axis is along the $x$ direction, $K^{xx} < 0$.

turn, decrease with increasing temperature. As the gap disappears, the system should transform into the spin spiral state in the plane perpendicular to the easy axis at finite temperature, analogously to what happens at zero temperature when the parameters in the Hamiltonian are modified.

The mean-field model described in section 4.3 can also account for such a phase transition; although the two-site anisotropy is replaced by the Dzyaloshinsky–Moriya interaction, these two terms are decoupled the same way during the mean-field approximation, which is different from the description of the on-site anisotropy. We performed the calculations for fixed values of the temperature, starting from a mean-field spin configuration

$$
\langle S_i \rangle = \left( \cos \left( \frac{\pi}{4} \right), \sin \left( \frac{\pi}{4} \right) \sin (k_0^y R_i^y), \sin \left( \frac{\pi}{4} \right) \cos (k_0^y R_i^y) \right). 
$$

(9.1)

Since in (9.1) the spins are located on a surface of a cone instead of being confined to a single plane as in the spin spiral state discussed in section 6.1, such a configuration is also known as a conical spin spiral. We calculated the magnetizations at different lattice points by solving (4.19) numerically, using fixed-point iteration and Newton’s method. The spherical integrations were performed by applying the Lebedev–Laikov quadrature[139]. The only simplification compared to the simulations was using a one-dimensional spin chain instead of the two-dimensional lattice: since all the spins are parallel in the considered spin spiral and ferromagnetic states when moving along the $x$ axis, we supposed that this remains the case in the mean-field model, and we only considered different values of $\langle S_i \rangle$ for spins along the $y$ axis. The length of the chain was $L = 64$ atoms. We performed the calculations for different wave vectors of $k_0$, and compared the values of the free energy from (4.18) to determine the correct equilibrium
state at a given temperature. This was necessary because spin spirals with different wave vectors may be metastable at the same temperature — see appendix B.6 for a detailed discussion.

From the calculations it turned out that the initial three-dimensional spin configuration never corresponds to a solution of the mean-field equation (4.19); the system always rotated to the ferromagnetic state in the *x* direction or to the spin spiral state in the *yz* plane depending on the temperature and the initial wave vector \( k_0 \). The spin spiral state with the wave vector minimizing (6.6), \( k_0^y \approx 0.093750 \frac{2\pi}{a} \), was the one which became stable at the lowest temperature, and it immediately represented a free energy minimum over the ferromagnetic state. Although spin spirals with different wave vectors also represented solutions of (4.19) at higher temperatures, they remained metastable with a higher free energy compared to the spin spiral with \( k_0^y \approx 0.093750 \frac{2\pi}{a} \) up until the transition into the paramagnetic state. This indicates that there is indeed a transition from the ferromagnetic state to the spin spiral state as the temperature is increased. When the simulations were started from a canted ferromagnetic state, \( k_0 = 0 \) in (9.1), the system converged to the ferromagnetic state along the *x* axis at all temperatures, indicating that it is a metastable state. This means that the phase transition is of first order in the mean-field model, which is in contradiction with the calculations at zero temperature in section 6.2.

We compared the results of the theoretical calculations to Monte Carlo simulations. The wave vector minimizing (6.6) with the model parameters mentioned above is \( k_0^y \approx 0.093750 \frac{2\pi}{a} \), which is an allowed wave vector on an \( N = 64 \times 64 \) lattice the simulations were performed on. The ferromagnetic and spin spiral phases were characterized by the static structure factor \( S^{\text{stat}}(k) \), calculated according to (7.5). We note that for a perfect sinusoidal spiral given by (6.1) one has \( S^{yy}(k_0) + S^{zz}(k_0) = 0.5 \) at zero temperature; to achieve a better comparison with the squared magnetization \( S^{zz}(k = 0) \), we multiplied this value by 2. This multiplication corresponds to calculating \( S^{yy}(k_0) + S^{zz}(k_0) + S^{yy}(-k_0) + S^{zz}(-k_0) \) due to the symmetry of the static structure factor with respect to \( k_0 \).

The results of simulations and mean-field calculations are shown in figure 9.9. As expected, mean-field theory significantly overestimates the critical temperature, but the qualitative agreement between simulation and theory is apparent from the figure. The Monte Carlo simulations in figure 9.9(b) point towards a continuous phase transition, and we did not observe hysteresis when sweeping through the transition region by increasing or decreasing the temperature. The most probable reason for the discrepancy in the order of the transition between theory and simulations is that during the mean-field calculations, we only consider some specific modifications of the spins, not all possible spin wave excitations. The ferromagnetic state may represent a local minimum in the phase space along some one-dimensional cross-sections, but this does not indicate that it is a real energy minimum in the many-dimensional space.

A possible explanation why this transition cannot be observed in the actual Fe/W(110) system is that the Dzyaloshinsky–Moriya is not sufficiently strong for such a transition, and two-site anisotropy terms such as the dipolar coupling also favour the in-plane ferromagnetic state over the out-of-plane direction. For an approximation on the parameter range where the transition is possible see appendix D.3.

We note that a phase transition from a conical spin state (9.1) to the spin spiral in the plane perpendicular to the ferromagnetic component can be observed in bulk Ho[140]. This transition is similar to the effect discussed in this section; however, the noncollinear
Figure 9.9: Static structure factor $S^{αα}(k)$, indicating a spin reorientation transition from the ferromagnetic state to the spin spiral state in the perpendicular plane as a function of temperature. The values are calculated from (a) mean-field theory and (b) Monte Carlo simulations. The wave vector $k_0^\parallel$ is given in $\frac{2\pi}{a}$ units. The simulation parameters are $J = -1, D = 0.349, K^{xx} = -0.12$ and $N = 64 \times 64$. The averaging was performed over a simulation length of $10^6$ steps after a thermalization of $10^5$ steps.
Figure 9.10: Sketch of a double-layer on the (110) surface of a bcc lattice, with the atoms in the different layers denoted by different colours. The $x, y$ and $z$ axes correspond to the [110], [001] and [110] crystallographic directions, respectively. The central atom 0 interacts with the nearest neighbours in the same layer and the nearest neighbours in the other layer. The intralayer coupling includes scalar Heisenberg exchange $J_1 = J_{1yy} = J_{1zz}$, Dzyaloshinsky–Moriya interaction $D$ with directions denoted in the figure, and two-site anisotropy $\Delta J_1 = J_{1xx} - J_{1yy} = J_{1xx} - J_{1zz} < 0$. Atoms in different layers interact with scalar Heisenberg exchange $J_2 = J_{2xx} = J_{2yy} = J_{2zz}$. The easy axis preferred by the on-site anisotropy is out-of-plane, $K^{zz} < 0$.

state of Ho is induced by the frustrated scalar Heisenberg exchange interactions instead of the Dzyaloshinsky–Moriya interaction, which is absent in the hcp crystal structure due to symmetry reasons.

9.4 Spin reorientation transition from the spin spiral state to the ferromagnetic state perpendicular to the spiral plane

In double-layer Fe on W(110), the reorientation transition happens in the opposite direction compared to section 9.3. A simple model which can reproduce this phenomenon is sketched in figure 9.10. It includes a ferromagnetic scalar Heisenberg exchange coupling between the nearest neighbours in the same layer $J_{1yy} = J_{1zz} = J_1 < 0$, as well as a ferromagnetic coupling between the nearest neighbours in the different layers $J_{2xx} = J_{2yy} = J_{2zz} = J_2 < 0$. The atoms in the different layers are actually closer than the ones in the same layer due to the relaxation of the Fe layers with respect to the W bulk and each other, which leads to $|J_2| > |J_1|$ – see figure 9.4(a). We also included a Dzyaloshinsky–Moriya interaction $D = (D, 0, 0)$ between the nearest neighbours in the same layer. Although the Dzyaloshinsky–Moriya vector may also have a $y$ component, we only kept
the $D_{ij}^z$ term, since this is responsible for the creation of cycloidal spin spirals with wave vector along the $y$ axis as it was discussed in section 6.2. We also included anisotropy terms which can account for the observed transition as discussed in section 4.3: since the easy axis is out-of-plane at low temperatures, this was described by $K^{zz} < 0$. The in-plane easy axis at high temperature was described by $J_1^{zz} - J_2^{zz} = J_1^{zz} - J_1^{yy} = \Delta J_1 < 0$, which includes the effect of the dipolar interactions, since they also prefer the in-plane orientation.

The parameters were chosen such a way to reproduce the out-of-plane ferromagnetic ground state determined from ab initio calculations in section 9.1: we set $J_1 = -1, J_2 = -2, D = 0.2, K^{zz} = -0.05$ and $\Delta J_1 = -0.023$. The mean-field calculations were performed the same way as in section 9.3, by starting from the conical spin configuration (9.1) and solving equation (4.19) to determine the spin configuration at a fixed temperature. By changing the wave vector of the original spin spiral state, the calculations did not always converge to the same solution, and we compared their free energies from (4.18) in this case to find the correct equilibrium state at finite temperature. Once again, we supposed during the mean-field calculations that the spins are parallel in the direction perpendicular to the spin spiral wave vector $k_0$, and used a spin chain consisting of $L = 256$ atoms. We also assumed that the spins in the different layers at the same position along the $y$ axis were parallel to each other; this was justified as the considered parameters of the Hamiltonian were symmetric with respect to exchanging the two layers. In the Monte Carlo simulations, we considered $32 \times 256$ atoms in both layers, with the longer side of the simulation box parallel to the $y$ direction.

The results are summarized in figure 9.11, characterizing the different ordered states by the static structure factor $S^{\alpha\beta}(k)$ (7.5) as before. Although the ground state is ferromagnetic along the $z$ direction, the system turns into a spin spiral state in the $yz$ plane at low temperature, then the wave vector of the spin spiral gradually increases. Within the terms of mean-field theory, this is explained by the different description of the on-site anisotropy and exchange terms such as the Dzyaloshinsky-Moriya interaction, which is also the cause of the reorientation transition. As the temperature is increased, the system gets closer to the harmonic spin spiral state minimizing the spin energy (6.6), which corresponds to $k_0^y \approx 0.031250 \frac{2\pi}{a}$ with the values of $J_1, J_2, D$ used in the simulations and the finite size of the lattice. For a more detailed discussion about the effect of the finite lattice size on the simulations the reader is referred to appendix B.6. The on-site anisotropy is sufficiently strong that the wave vector of the optimal harmonic spiral state is never reached during the simulations. This transition from the out-of-plane ferromagnetic state to a spin spiral state where the plane of the spiral contains the ferromagnetic direction is discussed in more detail in section 10.4 based on spin wave theory.

More importantly, the proposed model can also describe the reorientation from the spin spiral state into the ferromagnetic direction perpendicular to the plane of the spiral, which was also observed experimentally – see figures 9.1(c)-(d). This transition happens over a wide temperature range, with an intermediate state where the spins possess a finite magnetization along the $x$ direction, as well as a spiral structure in the $yz$ plane. However, this three-dimensional spin structure illustrated in figures 9.12-9.13 is different from the conical spin spiral of the initial condition (9.1). In the mean-field approximation shown in figure 9.12, the length of the magnetization vector,

$$\langle S_i \rangle = \sqrt{\langle S_i^x \rangle^2 + \langle S_i^y \rangle^2 + \langle S_i^z \rangle^2},$$

(9.2)
Figure 9.11: Static structure factor $S^{\alpha\alpha}(k)$, indicating a spin reorientation transition from the out-of-plane ferromagnetic state to the spin spiral state, then to the ferromagnetic state perpendicular to the spiral plane. The figures show the results of (a) mean-field theory and (b) Monte Carlo simulations. The wave vector $k_0^y$ is given in $\frac{2\pi}{a}$ units. The simulations were performed by starting from the ground state and increasing the temperature. The simulation parameters are $J_1 = -1, J_2 = -2, D = 0.2, K^{zz} = -0.05, \Delta J_1 = -0.023$ and $N = 32 \times 256 \times 2$. The averaging was performed over a simulation length of $10^6$ steps after a thermalization of $10^5$ steps.
Figure 9.12: Elliptic conical spin spiral state in real space. The magnetization components $\langle S_i^a \rangle$ are obtained from the self-consistent solution of the mean-field equations (4.19), while the length $\langle S_i \rangle$ is calculated from (9.2). The parameters are $J_1 = -1, J_2 = -2, D = 0.2, K^{zz} = -0.05, \Delta J_1 = -0.023, k_B T = 0.7$ and $L = 256$.

Figure 9.13: Elliptic conical spin spiral state in reciprocal space. The static structure factor $S^{aa}(k)$ is obtained from Monte Carlo simulations, shown as a function of the wave vector $k^y$, for $k^x = 0$. The simulation parameters are $J_1 = -1, J_2 = -2, D = 0.2, K^{zz} = -0.05, \Delta J_1 = -0.023, k_B T = 0.4$ and $N = 32 \times 256 \times 2$. 
depends only slightly on the lattice point \( i \), so the spin structure may still be accurately described by magnetization vectors of the same length. However, these magnetization vectors are localized on an elliptic cone, where the long axis of the ellipse is along the \( z \) direction, since this is energetically preferable to the \( y \) direction. Due to the fixed magnetization length, the \( x \) component of the spins is also modulated, but the modulation wave vector is twice as large as the spiral wave vector \( k_0^y \), since the \( x \) component assumes the same value after performing a \( \pi \) rotation along the ellipse, not only after a \( 2\pi \) rotation. This modulation is visible in the static structure factor obtained from Monte Carlo simulations in figure 9.13: while the \( S^{yy} \) and \( S^{zz} \) components are modulated with \( k_0^y = 0.023438 \frac{2\pi}{a} \), in the \( S^{xx} \) component the spin spiral peak is located at \( 2k_0^y = 0.046875 \frac{2\pi}{a} \), besides the high \( S^{xx}(k) \) value at \( k = 0 \) describing the ferromagnetic component.

The presence of such a modulated three-dimensional state was already suggested in [92, 93] based on a micromagnetic model at zero temperature. The model included the same types of interactions as our lattice model, except that the two-site anisotropy was replaced by another on-site one, which leads to an equivalent description if temperature effects are ignored. Although low-temperature measurements[19] rule out the presence of such an elliptic conical spiral state as the ground state of Fe double-layer on W(110), the reorientation transition in [20] was only characterized by the disappearance of the out-of-plane magnetized stripes, which allows for a presence of a canted intermediate state. We also point out that the presence of the Dzyaloshinsky–Moriya interaction and the two types of anisotropies are all necessary for the appearance of a continuous phase transition over a wide temperature range. Without the Dzyaloshinsky–Moriya interaction, the spin reorientation transition is instantaneous as it was discussed in section 4.3. In double-layers, the transition may become continuous if different on-site anisotropy constants are considered in the different layers – see section 9.2 and [81] –, but we could describe the continuous transition without this extension of the model. Without the anisotropy in the spiral plane, the transition is again instantaneous as was demonstrated in section 9.3, since the stability regime of the three-dimensional state collapses to a single point in this case. The anisotropy term perpendicularly to the spiral state is also necessary, since this drives the system towards the reorientation transition.

Finally, we also mention that the presence of an intermediate conical state over a wide temperature range has also been demonstrated in Co/Pt multilayers[141-143]. However, the driving mechanism behind this continuous transition was identified as a higher-order anisotropy term instead of the Dzyaloshinsky–Moriya interaction. Since the axis of the cone is out-of-plane in the mentioned measurements, it should be perpendicular to the direction of the Dzyaloshinsky–Moriya vectors, even though the latter were not considered in the models of Co/Pt. In our case, the axis of the cone is in-plane and parallel to the Dzyaloshinsky–Moriya vectors, and the spin components in the plane perpendicular to the cone axis represent a spin spiral with a given rotational sense. In comparison, the spin components perpendicular to the cone axis do not show any identifiable pattern[141] in Co/Pt, since the plane they are located in is close to being isotropic.
Chapter 10

Fe monolayer on Ta(110): spin spiral phases and phase transitions

There are numerous experimental and theoretical data available for ultrathin films consisting of $3d$ elements other than Fe on the same W(110) substrate as in chapters 8-9. The Mn monolayer is ordered in a planar spin spiral ground state with wave vector along the [110] direction[10], while the double-layer shows a complex spin spiral order with spins located on a double cone, and the spiral wave vector parallel to the [001] axis[144]. The Cr monolayer also has a spin spiral ground state, with the wave vector in the [001] direction[88, 145].

On the other hand, significantly less attention has been paid to the case when the substrate is replaced instead of the magnetic layer. Ta has one less electron than W, and it also forms a bcc lattice structure. For example, the scanning tunnelling microscopy image of W and Ta (110) surfaces was calculated using ab initio methods in [146], but only the former was compared to experiments.

Ab initio calculations for an Fe monolayer on the (100) surface of $W_{1-x}Ta_x$ ($0 \leq x \leq 1$) alloys were performed in [147, 148]. As illustrated in figure 10.1, it was found that the magnetic ground state is a two-sublattice Néel antiferromagnetic state on pure W, and it changes to ferromagnetic on pure Ta, while a row-wise antiferromagnetic phase is preferable over both states for intermediate concentrations. The different lattice constant of the atoms, $a_{Ta} = 3.301 \text{ Å}$ and $a_{W} = 3.165 \text{ Å}$, has two effects on the geometry of the alloys. It must be taken into account in determining the lattice constant of the alloy as it was done in [147, 148], but it also influences the distance between the Fe monolayer and the substrate. Including this relaxation effect, it was shown in [149] that the ground state of Fe monolayer on Ta(100) substrate should be row-wise antiferromagnetic.

In this chapter, the results of ab initio calculations will be discussed for an Fe monolayer on Ta(110) based on the general algorithm in sections 7.1 and 7.3. Depending on the distance between the magnetic layer and the substrate, we identify three different types of spin spiral states as possible ground states of the system, beyond the out-of-plane ferromagnetic state. It will be demonstrated that the system may also switch between the different ground states as the temperature is increased. These phase transitions will be explained by using spin wave expansion from section 4.2 and mean-field theory from section 4.3.
Figure 10.1: Comparison of different magnetic configurations of Fe monolayer on $W_{1-x}Ta_x(100)$ surface, from [147]. (a) Two-sublattice Néel antiferromagnetic, row-wise antiferromagnetic and ferromagnetic spin configurations. (b) Total energy of the states depicted in (a) as a function of Ta concentration $x$.

10.1 Calculated exchange interactions and ground states

The ab initio calculations were performed similarly to W substrate; details are given in appendix D.1. Since the mismatch between the lattice constants is even larger in the case of Fe on Ta than for Fe on W, it is expected that the relaxation of the top Fe layer with respect to the substrate also becomes larger. However, we have found no previous experimental or theoretical data for the layer relaxations in the considered system; therefore, we considered values from the 10%-17% range, the same as in the case of W substrate. The relaxation between the substrate layers was neglected as before.

The calculated exchange interactions appearing in the Hamiltonian (3.1) are summarized in figure 10.2. Using the same coordinate system as in chapters 8 and 9, the [110], [001] and [110] directions were identified with the $x$, $y$ and $z$ axes, respectively. The strongest interaction is the ferromagnetic coupling between the next-nearest neighbours at distance 1.0 $a_{in}$ from each other. However, this interaction only couples spins in a chain along the [001] direction, and is insufficient for the stabilization of the ferromagnetic ground state as will be shown below. Although the nearest-neighbour exchange interaction is ferromagnetic, its magnitude decreases with increasing relaxation, competing with the increasingly antiferromagnetically coupled third and fifth neighbours. The Dzyaloshinsky–Moriya interactions are weaker than in Fe monolayer on W(110) (cf. figures 9.3(b)-(c)), and they prefer left-rotating cycloidal spin spirals or Néel domain walls according to the definitions in sections 6.1 and 6.3.

The ground state was obtained from zero-temperature spin dynamics simulations, by preparing the system in different initial configurations and comparing the energy after relaxation of the spins. The results are summarized in figures 10.3-10.5. Although the ground state is out-of-plane ferromagnetic below 10.5% relaxation, it transforms into a spin spiral state SS I at this point, to another spin spiral state SS II at 13.8% relaxation, and finally to the SS III spin spiral state at 14.5% relaxation. The SS I and SS II
Figure 10.2: Calculated (a) scalar Heisenberg exchange interactions (2.39) and (b)-(c) Dzyaloshinsky–Moriya vector components (2.37) for Fe monolayer on Ta(110) surface, for different relaxation values. For the Dzyaloshinsky–Moriya vectors, displayed are the values for the pairs with $R_{ij}^0 > 0$ and $R_{ij}^1 > 0$, while for the rest of the pairs they may be obtained from the symmetry relations described in appendix D.2. Multiple data points at the same distance denote neighbours not connected by symmetry.

Figure 10.3: Phase diagram of Fe monolayer on Ta(110) substrate. Shown are the energies per spin of ferromagnetic (FM) orientations along different crystallographic axes, of two different cycloidal spin spiral states (SS I and SS II) discussed in the text, as well as the ground state energy (GS).
states correspond to left-rotating cycloidal spin spirals with wave vectors along the [110] direction. Since the [110] direction remains the hard axis throughout the whole considered relaxation range, the spin spirals become distorted due to the anisotropy. This is best visible in figure 10.4(b) for the SS I state.

The ground state energy of the anharmonic spiral is approximated by the energy of the perfectly sinusoidal spin spiral configuration,

\[ S_i = (-\sin(k_0^x R_i^x), 0, \cos(k_0^x R_i^x)) \].

The energy of such spin configurations is shown in figure 10.5, compared to the out-of-plane ferromagnetic state for different relaxation values. The functions do not converge to 0 as \( k_0^x \rightarrow 0 \), since the anisotropy energy of the harmonic spin spiral state is different from that of the ferromagnetic state – see the discussion after (B.69) in appendix B.5. Figure 10.3 indicates that the harmonic spin spiral energies denoted by SS I and SS II are good approximations for the energies of the relaxed, anharmonic spiral ground states (GS) in the SS I and SS II phases.

Figure 10.5 also expresses the difference between the SS I and SS II states. Although the wave vector \( k_0 \) of the spin spiral continuously changes in the SS I state, the system jumps to a completely different energy minimum at 13.8% relaxation, corresponding to a first-order phase transition. The spin dynamics simulations shown in figures 10.3-10.4 were performed on an \( N = 64 \times 64 \) lattice, and the spin spiral energies in figure 10.5 were calculated for the wave vectors allowed by the periodic boundary conditions on the same lattice size.

Although the Dzyaloshinsky–Moriya interaction plays a role in the transition from the ferromagnetic to the SS I state and in the determination of the rotational sense of the spiral, the transition from the SS I to the SS II state is due to the frustrated nature
Figure 10.5: Spin spiral energies per spin relative to the energy of the ferromagnetic state, calculated from the Heisenberg model parameters in the harmonic left-rotating cycloidal spin spiral configuration (10.1) for wave vectors $k^x_0$ along the $[\bar{1}10]$ direction, given in units of $\frac{2\pi}{\sqrt{2}\eta_{\text{TS}}}$. The points at which the spin spiral energies are calculated in figure 10.3 are denoted by squares for SS I and circles for SS II. The inset shows a magnified view of the range $0 \leq k^x_0 \leq 0.15$.

of the scalar Heisenberg exchange interactions along the $x$ axis – see figure 10.2(a). The weakness of the Dzyaloshinsky–Moriya interaction is even more apparent in the SS III state. Since the $x$ axis remains the hard axis of the system, the anisotropy prefers a rotation of the spins in the $yz$ plane, while the Dzyaloshinsky–Moriya interaction prefers cycloidal spin spirals in the $xz$ plane. At 14.5% relaxation, the Dzyaloshinsky–Moriya interaction can no longer force the system into the cycloidal state, and the chirality vector $\chi$, which is perpendicular to the plane of the spiral as mentioned in section 6.1, starts rotating in the $xy$ plane. This describes the difference between the SS II and the SS III states, while the wave vector basically does not change during the transition.

### 10.2 Finite-temperature phase transitions

At relaxation values close to the phase transition points in figure 10.3, the energy difference between the ground states visualized in figure 10.4 is small, and it can be expected that a phase transition also occurs as a function of temperature for a fixed relaxation value. Therefore, we performed Monte Carlo simulations on an $N = 64 \times 64$ lattice for different relaxation values close to the three transition points.

The results of the simulations are summarized in figure 10.6. As in chapter 9, the different phases have been characterized by the static structure factor $S^{\alpha\alpha}(\mathbf{k})$ (7.5). For the first two phase transitions, we have calculated the sum over the Descartes components $S(\mathbf{k})$ (7.6), since the $yz$ plane of the rotation did not change, only the wave vector of the spiral. As it was described in section 9.3, for finite wave vectors the $S^{\alpha\alpha}(\mathbf{k})$ and $S^{\alpha\alpha}(−\mathbf{k})$ values were summed up, in order to obtain the same normalization as the homogeneous
Figure 10.6: Component-resolved $S^{\alpha\alpha}(k)$ and summed up $S(k)$ static structure factor as a function of temperature, obtained from Monte Carlo simulations performed for Fe monolayer on Ta(110) for different relaxation values. The figures show (a) the FM–SS I transition at 10% relaxation; (b) the SS II–SS I transition at 13.8% relaxation; and (c) the SS III–SS II transition at 15% relaxation. The wave vector $k^*_0$ is given in $\frac{2\pi}{\sqrt{2a_{Ta}}}$ units. The simulations were performed by initializing the system in the ground state and increasing the temperature. The lattice size was $N = 64 \times 64$. The averaging was performed over a simulation length of $10^6$ steps after a thermalization of $2 \times 10^5$ steps.
Figure 10.7: Sketch of the (110) surface of a bcc lattice. The $x$, $y$ and $z$ axes correspond to the [110], [001] and [110] crystallographic directions, respectively. The central atom 0 interacts via scalar Heisenberg exchange coupling with several atoms that have different positions along the $x$ axis, denoted by $J_1, J_2, J_3, J_5$ and $J_{11}$. The Dzyaloshinsky–Moriya interaction $D$ with directions shown in the figure is considered between the nearest neighbours. Equivalent neighbours are formed by mirroring on the $xz$ and $yz$ planes: there are four neighbours of types 1 and 7, as well as two neighbours of types 2, 3 and 11. The Dzyaloshinsky–Moriya vector $D$ transforms as an axial vector. The on-site anisotropy prefers the out-of-plane easy axis $K^{zz} < 0$, and suppresses the hard direction along the $x$ axis, $K^{xx} > 0$.

$k_0 = 0$ case at zero temperature.

At 10% relaxation, the system turns from a ferromagnetic phase into the SS I phase around $T_{\text{trans}} \approx 120 \, \text{K}$, then the wave vector of the spiral gradually increases until a maximal value before reaching the paramagnetic phase at $T_c \approx 210 \, \text{K}$. Such a transition has already been described in section 9.4 within mean-field theory, where the different temperature dependence of the on-site and exchange terms was responsible for the appearance of the spiral state. Figure 10.6(b) shows a transition from the high wave vector SS II phase to the low wave vector SS I state at $T_{\text{trans}} \approx 120 \, \text{K}$ below the transition to the paramagnetic state, $T_c \approx 140 \, \text{K}$. Finally, figure 10.6(c) indicates the rotation of the spin spiral chirality vector $\chi$ as a function of temperature. At $T_{\text{trans}} \approx 80 \, \text{K}$, the $y$ component of the spins disappears, corresponding to the transition to the cycloidal SS II state from the SS III state, while the paramagnetic state is reached at $T_c \approx 210 \, \text{K}$.

10.3 Model Hamiltonian and its equilibrium states

To achieve a better understanding of the ground states and phase transitions, we once again relied on a model Hamiltonian. The interactions are depicted in figure 10.7. For the ferromagnetic and SS I states, it is sufficient to consider nearest-neighbour ferromagnetic scalar Heisenberg exchange $J_1 < 0$, Dzyaloshinsky–Moriya interaction $D_{ij} = (0, D_{ij}, 0)$ and easy-axis on-site anisotropy $K^{zz} < 0$. Similarly to section 9.4, the direction of the nearest-neighbour Dzyaloshinsky–Moriya vectors is not fixed by symmetry considerations within the $xy$ plane. However, we only include the $y$ component since this will influence the energy of spin spirals with wave vectors along the $x$ direction – see section 6.1. For the SS II state, one has to include scalar Heisenberg exchange interactions in the model with at least four neighbours with different coordinates along the $x$ direction to
Figure 10.8: Spin wave spectrum around a spin spiral state with wave vector $k^x_0 = 0.062500 \frac{2\pi}{\Delta a_{31}}$. The parameters are $J_1 = -2 \text{mRy}$, $D = 0.4 \text{mRy}$ and $K^{zz} = 0 \text{mRy}$, in which case the SS I configuration is the ground state.

qualitatively reproduce the curve shown in figure 10.5; therefore, we will use $J_1$, $J_3$, $J_7$ and $J_{11}$. The scalar Heisenberg couplings are summed up along the $y$ axis: for example, $J_3$ represents the coupling between the spin at site 0 and all the atoms which have the same $x$ coordinate as the third neighbours. This is justified because the contributions of these Fe-Fe pairs appear additively with the same geometric factor in the energy of spin spirals with wave vectors along the $x$ axis. Finally, the rotation of the spiral plane in the SS III phase can be accounted for by introducing a hard axis along the $x$ direction, which counteracts the Dzyaloshinsky–Moriya interaction that prefers cycloidal spin spirals. The scalar Heisenberg exchange interaction $J_2 < 0$ is only used to stabilize the states, by forcing the spins along the $y$ axis to remain parallel.

We will describe the transition between the ferromagnetic and SS I states, as well as between the SS II and SS I states using the spin wave expansion method described in section 4.2. For this we have to determine the equilibrium anharmonic spin spiral configurations and the spin wave spectra around them numerically -- for the detailed algorithms see appendices B.5 and D.4.

For $K^{zz} = 0$, the spiral is harmonic, and the spectrum is given by (6.8)-(6.10); this is illustrated for the SS I state in figure 10.8. Compared to the spectrum of the ferromagnetic state, figure 8.3 in section 8.1, the qualitative difference is that the gap is absent in the spin spiral state. As it was discussed in section 6.3, this is a consequence of the spontaneous breaking of a $U(1)$ symmetry corresponding to the displacement of the spiral in the wave vector direction, and introducing a finite value of $K^{zz}$ does not remove this Goldstone mode. However, this symmetry is absent in the ferromagnetic state, and $K^{zz}$ will introduce a gap. If the ferromagnetic state has lower energy $E_0 < E'_0$ compared to the spin spiral state, it will represent the ground state of the system. However, at high wave vectors the spectrum of the ferromagnetic state and the spin spiral states is similar, while the gap increases the spin wave energies at low wave vectors, indicating $\sum_k \ln \omega_k > \sum_k \ln \omega'_k$ with the notations introduced in section 4.2. This means that spin wave expansion predicts a transition from the ferromagnetic to the SS I state as

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$$k_0^2 (\frac{2\pi}{\sqrt{2}\delta_{2D}}) \quad \lambda (\text{nm}) \quad E_0/N (\text{mRy}) \quad F_{SW}/Nk_B T \quad T_{\text{trans}}^{\text{free}} (K)$$

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Table 10.1: Energy ($E_0/N$), free energy correction ($F_{SW}/Nk_B T = \sum_k \ln \omega_k/N$) per spin and transition temperature ($T_{\text{trans}}^{\text{free}}$, (4.13)) for different wave vectors $k_0^2$ and corresponding wavelengths $\lambda$ for the transition from the ferromagnetic to the SS I state, calculated for a lattice size of $N = 128 \times 64$ atoms with periodic boundary conditions.

$$T_{\text{trans}} (K) \quad T_{\text{trans}}^{\text{free}} (K) \quad T_c (K)$$

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Table 10.2: Transition temperatures for different wave vectors $k_0^2$ and corresponding wavelengths $\lambda$, calculated for a lattice size of $N = 64 \times 32$ with periodic boundary conditions. $T_{\text{trans}}$ and $T_{\text{trans}}^{\text{free}}$ indicate the temperature where the SS I state with the given wave vector becomes the global minimum of the free energy derived from perturbation theory (4.9) and for free spin waves (4.12). $T_c$ is the temperature where the state becomes unstable according to perturbation theory.

As we will see, the theory also correctly determines the direction of the transition between the SS I and the SS II states, although there is no such simple qualitative argument in that case, since both considered spectra are ungapped.

As has been mentioned in section 4.2, the transition into the paramagnetic state may be described by introducing perturbative corrections into the calculations on the basis of (4.9). Compared to this perturbative method, we will refer to the transition temperature determined from (4.13) as free spin wave theory.

10.4 Transition from the ferromagnetic to the SS I state

For the description of the transition from the ferromagnetic to the SS I state, we used the model parameters $J_1 = -2.0 \text{mRy}, D = 0.4 \text{mRy}$ and $K^{zz} = -0.22 \text{mRy}$. With these coupling coefficients, the spin spiral energy curve shown in figure 10.5 will have a single minimum away from $k_0 = 0$, but this minimum will be energetically unfavourable compared to the out-of-plane ferromagnetic state.

The results of spin wave expansion performed for free spin waves (4.12) are summarized in table 10.1. The expansion was carried out around the exact anharmonic equilibrium spin spiral state. As it was expected, the energy of the equilibrium state
Figure 10.9: Free energy difference between spin spiral states with different wave vectors, calculated from free spin wave theory (4.12) and from perturbation theory (4.9). The line at $\Delta F/N = 0$ is a guide to the eye.

increases with increasing wave vector $k_\parallel$, but the correction to the free energy from the spin waves, $\sum_k \ln \omega_k / N$ in (4.12), decreases. Based on (4.13), this means that the ferromagnetic state will turn into a spin spiral state at finite temperature, then the wave vector of the spiral will keep increasing. Since the jumps in the wave vector of the spin spiral are simply a consequence of the finite size of the lattice, only moving from the ferromagnetic state to the spin spiral state with the lowest allowed wave vector can be considered a real phase transition.

One shortcoming of spin wave expansion based on free spin waves is that all the equilibrium states remain stable up to arbitrarily large temperatures. Therefore, we included perturbative corrections in the calculations, which also give a prediction for the transition temperature $T_c$ into the paramagnetic state as it was discussed in section 4.1. If a predicted transition temperature $T_{\text{trans}}$ is higher than the critical temperature, then a spin spiral with such a wave vector probably cannot be observed during the simulations or the experiments. The results of perturbation theory are summarized in table 10.2. Note that the difference in the $T_{\text{trans}}$ values between tables 10.1 and 10.2 is a consequence of the different lattice sizes used for the calculations, which influences the allowed wave vectors, as well as the spin wave frequencies. Besides providing an approximation for the critical temperature, the perturbative corrections naturally also modify the predictions for $T_{\text{trans}}$, notably increasing its value for the transition from the ferromagnetic to the spin spiral state. These results are also depicted in figure 10.9. The free energy difference curves calculated from perturbation theory end at a temperature where one of the considered equilibrium states loses its stability; in comparison, the free energy difference calculated from free spin waves corresponds to a linear function, which can be continued up to arbitrarily high temperatures.

The Monte Carlo simulation results in figure 10.10 performed for the model Hamilto-
Figure 10.10: Static structure factor $S(k)$ as a function of temperature, obtained from Monte Carlo simulations performed on the model Hamiltonian. The simulations were carried out at (a) increasing and (b) decreasing temperature, showing strong hysteresis. The wave vector $k_0^x$ is given in $\frac{2\pi}{\sqrt{2aT}}$ units. The simulation parameters are $J_1 = -2.0\text{mRy}, D = 0.4\text{mRy}, K^{zz} = -0.22\text{mRy}$ and $N = 128 \times 64$. The averaging was performed over a simulation length of $10^6$ steps after a thermalization of $10^5$ steps.
nian show good agreement with the calculations based on ab initio coupling coefficients, figure 10.6(a), as well as the spin wave expansion calculations discussed above. The transition point to the paramagnetic state $T_c$ is well approximated by perturbation theory: for the $k_0^2 = 0.062500 \frac{2\pi}{\sqrt{2\omega_{\text{ps}}}}$ spiral state, it predicts $T_c = 261.7\, \text{K}$, while the critical temperature from the simulation is around 220 K. For comparison, from the random phase approximation\cite{68}, one obtains $T_c = 271.1\, \text{K}$ for the critical temperature of the ferromagnetic state, while the mean-field approximation overestimates this temperature by a significantly larger amount – see sections 9.3-9.4 for examples. On the other hand, the estimated transition temperature from the ferromagnetic to the spin spiral phase is $T_{\text{trans}} \approx 120\, \text{K}$ in the simulations, which is significantly higher than the prediction of spin wave theory. It should be noted that including the perturbative corrections shifts $T_{\text{trans}}$ closer to the value obtained from the simulations – see figure 10.9. However, the main reason for the discrepancy between simulation and theory is probably that the transition happens between different metastable states, which leads to hysteresis in the simulations. This can be visualized by also performing the simulations at decreasing temperature: when the system starts from the paramagnetic phase and is cooled down to zero temperature, it freezes into the spin spiral state with wave vector $k_0^2 = 0.062500 \frac{2\pi}{\sqrt{2\omega_{\text{ps}}}}$, which is not the ground state of the system. A detailed discussion about metastable states with very long lifetimes in the finite-sized lattice is given in appendix B.6.

### 10.5 Transition from the SS II to the SS I state

For the modelling of the SS II–SS I transition, one requires several different scalar Heisenberg exchange interactions such that the spin spiral energy curve in figure 10.5 has two distinct minima $k_0, k_0' \neq 0$. As it was mentioned in section 10.3, the minimal number of scalar Heisenberg exchange coefficients equals four in this case, and the dependence of the energy on the wave vector could be relatively well reproduced by the choice $J_1 = -2.0\, \text{mRy}, J_2 = 2.58\, \text{mRy}, J_7 = -1.0\, \text{mRy}$ and $J_{11} = 0.8\, \text{mRy}$ in figure 10.7. The ground state is located at high wave vector $k_0^2 = 0.593750 \frac{2\pi}{\sqrt{2\omega_{\text{ps}}}}$, with a slightly higher local minimum at $k_0'^2 = 0.156250 \frac{2\pi}{\sqrt{2\omega_{\text{ps}}}}$. As the Dzyaloshinsky–Moriya interaction is necessary for the metastability of the spin spiral state with wave vector $k_0'^2$ – see (6.10) in section 6.2 –, we chose a value of $D = 0.4\, \text{mRy}$ between the nearest neighbours. On the other hand, on-site anisotropy terms are irrelevant for the current transition and were omitted from the model.

The results of spin wave expansion based on free spin waves are summarized in table 10.3, for a lattice size of $N = 128 \times 64$. The theory predicts a transition from the high wave vector state to the low wave vector one. This is in agreement with the Monte

<table>
<thead>
<tr>
<th>$k_0^2$</th>
<th>$\lambda$ (nm)</th>
<th>$E_0/N$ (mRy)</th>
<th>$F_{\text{SW}}/Nk_BT$</th>
<th>$T_{\text{trans}}$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.593750</td>
<td>0.79</td>
<td>-2.9894</td>
<td>1.4779</td>
<td>0.0</td>
</tr>
<tr>
<td>0.156250</td>
<td>2.99</td>
<td>-2.9736</td>
<td>1.4168</td>
<td>40.8</td>
</tr>
</tbody>
</table>

Table 10.3: Energy ($E_0/N$), free energy correction ($F_{\text{SW}}/Nk_BT = \sum_k \ln \omega_k/N$) per spin and transition temperature ($T_{\text{trans}}$) values as in table 10.1 for different wave vectors $k_0^2$ and corresponding wavelengths $\lambda$ for the SS II–SS I transition, on a lattice of size $N = 128 \times 64$ with periodic boundary conditions.
Figure 10.11: Static structure factor $S(k)$ as a function of temperature, obtained from Monte Carlo simulations performed on the model Hamiltonian. The simulations were carried out by initializing the system in the ground state and increasing the temperature. The wave vector $k_0^*$ is given in $\frac{2\pi}{\sqrt{2}a_{Pl}}$ units. The simulation parameters are $J_1 = -2.0\, \text{mRy}, J_3 = 2.58\, \text{mRy}, J_7 = -1.0\, \text{mRy}, J_{11} = 0.8\, \text{mRy}, D = 0.4\, \text{mRy}$ and $N = 128 \times 64$. The averaging was performed over a simulation length of $10^6$ steps after a thermalization of $10^5$ steps.

Monte Carlo simulations presented in figure 10.11, although the transition temperature is underestimated, taking the value $T_{\text{trans}} \approx 100\, \text{K}$ in the simulations. The results are also in agreement with the simulations performed using the *ab initio* coupling coefficients in figure 10.6(b).

### 10.6 Transition from the SS II to the SS III state

The transition from the SS II to the SS III state is characterized not by the change in the wave vector of the spin spiral state, but by the rotation of the chirality vector $\chi$ of the spiral away from the $y$ axis, corresponding to the cycloidal state, towards a direction in the $xy$ plane. The angle between $\chi$ and the $y$ axis coincides with the angle $\varphi$ between the plane of the spin spiral and the $xz$ plane, illustrated in figure 10.12. The rotation of the spiral plane can be understood from a model which treats the Dzyaloshinsky–Moriya interaction and the anisotropy terms as perturbations. In this case, the scalar Heisenberg exchange interactions are responsible for creating a harmonic spiral ground state in the system with wave vector $k_0$. For the anisotropy we chose $K^{xy} > 0$ and $K^{zz} = 0$, since *ab initio* calculations indicated that at 15% relaxation the ferromagnetic states along the $y$ and $z$ axes have almost the same energy, while the $x$ axis is a hard direction. The energy contribution per spin from the Dzyaloshinsky–Moriya interaction
and the anisotropy terms can be expressed as

$$\frac{\Delta E}{N} = \frac{1}{2}iD_{k_0} \cos \phi + \frac{1}{2}K^{xx} \cos^2 \phi, \quad (10.2)$$

with

$$-iD_{k_0} = 4D \sin \left( \frac{\sqrt{2}}{2}a_{tn}k_0^2 \right) \cos \left( \frac{1}{2}a_{tn}k_0^2 \right). \quad (10.3)$$

Differentiating (10.2) with respect to $\phi$ leads to the stationary points

$$\sin \phi^{(1)} = 0, \quad (10.4)$$

$$\cos \phi^{(2)} = -\frac{iD_{k_0}}{2K^{xx}}. \quad (10.5)$$

Substituting the solutions into (10.2) yields

$$\frac{\Delta E^{(1)}}{N} = \pm \frac{1}{2}iD_{k_0} + \frac{1}{2}K^{xx}, \quad (10.6)$$

$$\frac{\Delta E^{(2)}}{N} = -\frac{(-iD_{k_0})^2}{8K^{xx}}, \quad (10.7)$$

implying that whenever the second stationary point exists,

$$\left| \frac{-iD_{k_0}}{2K^{xx}} \right| < 1, \quad (10.8)$$

it will correspond to the minimum of the energy. This describes the rotation of the spiral chirality vector away from the $y$ axis when the Dzyaloshinsky–Moriya interaction is weak compared to the anisotropy. Note that the rotation of the spiral plane is only possible because the spiral is created by the frustrated scalar Heisenberg exchange interactions; purely ferromagnetic exchange interactions lead to either a ferromagnetic or a cycloidal spin spiral ground state as it was discussed in section 6.3.

For the present simulations the exchange parameters $J_1 = -2.0 \text{mRy}$, $J_3 = 3.0 \text{mRy}$ and $J_7 = -1.0 \text{mRy}$ were chosen, which create a spin spiral ground state with wave vector along the $x$ axis, $k_0^x = 0.546875 \frac{2\pi}{20\text{Ry}}$. We considered $D = 0.05 \text{mRy}$ between the nearest neighbours and $K^{xx} = 0.2 \text{mRy}$, and found that these values did not influence the shape of the spiral considerably, but confined the chirality vector to a general direction in the $xy$
plane, as shown in figures 10.4(d) and 10.12. We also included a ferromagnetic coupling in the calculations between the neighbours in the $y$ direction, $J_2 = -2.0 \text{mRy}$, which does not influence the spiral state, but removes the possible domain walls from the system along the $y$ axis. These domain walls occur because (10.5) has two solutions $\pm \varphi^{(2)}$ with the same energy; therefore, if the spins are weakly coupled along the $y$ direction, domains with angles $\varphi^{(2)}$ and $-\varphi^{(2)}$ may be simultaneously present in the system.

Calculating the spin wave spectrum reveals that only one of the states is stable for any value of $D$ and $K^{xx}$; therefore, the spin wave expansion is not suitable for describing this type of transition. However, the rotation from the SS III state to the SS II state can be understood within the terms of the mean-field theory discussed in section 4.3: analogously to the reorientation transition in section 9.3, the state preferred by the Dzyaloshinsky–Moriya interaction becomes favourable at higher temperature. This means that the angle defined by (10.5) will decrease as a function of temperature until (10.8) no longer holds.

For the mean-field calculations, we utilized a spin chain of length $L = 128$, where it was assumed that the spins perpendicular to the wave vector direction were parallel to each other – see sections 9.3 and 9.4. The initial configuration of the chain was a sinusoidal spiral with a rotated chirality vector,

$$\langle \mathbf{S}_i \rangle = \left( -\cos \left( \frac{\pi}{3} \right) \sin \left( k_0^x R_i^x \right), -\sin \left( \frac{\pi}{3} \right) \sin \left( k_0^x R_i^x \right), \cos \left( k_0^x R_i^x \right) \right). \quad (10.9)$$

The magnetization values were calculated from the self-consistent solution of (4.19) as usual. There was no reason to assume that the wave vector of the spiral would change during the process, and we only considered the value $k_0^y = 0.546875 - \frac{2\pi}{\sqrt{2}a_{\text{ns}}}$.

The results of mean-field theory and Monte Carlo simulations are compared in figure 10.13, showing good qualitative agreement. As expected, the chirality vector rotates towards the $y$ axis, corresponding to the cycloidal spin spiral configuration of the SS II state. This is in agreement with the results using the $ab \text{ initio}$-parametrized Hamiltonian in figure 10.6(c).
Figure 10.13: Component-resolved static structure factor $S^{\alpha\alpha}(k)$ as a function of temperature, calculated by using a model Hamiltonian. The figures show the results of (a) mean-field theory and (b) Monte Carlo simulations. The wave vector $k_0^z$ is given in $\frac{2\pi}{\sqrt{2a_{\text{ps}}}}$ units. The numerical simulations were performed by initializing the system in the ground state and increasing the temperature. The simulation parameters are $J_1 = -2.0 \text{ mRy}, J_2 = -2.0 \text{ mRy}, J_3 = 3.0 \text{ mRy}, J_7 = -1.0 \text{ mRy}, D = 0.05 \text{ mRy}, K^{xx} = 0.2 \text{ mRy}$ and $N = 128 \times 64$. The averaging was performed over a simulation length of $10^6$ steps after a thermalization of $10^5$ steps.
Chapter 11

Fe monolayer on Ir(111) with Pd overlayer: fluctuations and skyrmion lifetime

Besides the spin spiral states presented in the previous two chapters, the Dzyaloshinsky-Moriya interaction may contribute to the appearance of other noncollinear spin configurations such as magnetic skyrmion lattices discussed in section 6.4. The presence of a skyrmion lattice state was experimentally first verified in the cubic B20 system MnSi[11], where it was identified with the previously known A phase. Since the presence of interactions responsible for the creation of skyrmions is determined by the symmetry of the system, the skyrmion lattice phase has also been identified in several other bulk magnets with B20 symmetry such as FeGe[150, 151], FeCoSi[152, 153] and Cu3OSeO3[154]. Compared to the symmetry, the conduction properties of the system play a less important role in the creation of the skyrmion lattice phase, since the above mentioned materials include metals, half-metals and insulators. Skyrmion lattices have also been explored in other bulk materials such as Co-Zn-Mn alloys[155] and GaV₃S₈[156]. The latter compound has $C_{nv}$ symmetry in contrast to the $D_{n}$ symmetry of the previous ones, which leads to a different orientation of the Dzyaloshinsky-Moriya vectors[22] and a different phase diagram.

As it was mentioned in section 6.1, the $C_{nv}$ symmetry class is common in ultrathin film systems and multilayers made of otherwise inversion-symmetric materials; the Fe mono- and double-layers on W and Ta (110) surfaces with $C_{2v}$ symmetry discussed in the previous chapters provide an example for this argument. The skyrmion lattice phase in this symmetry class was first identified in a monolayer of Fe on Ir(111) substrate with a Pd overlayer using spin-polarized scanning tunnelling microscopy experiments[23]. Without the Pd layer, Fe monolayer on Ir(111) displays a so-called nanoskyrmion lattice ground state even in the absence of external magnetic field[157]; however, this state is different from the real hexagonal skyrmion lattice as the constituents are half-skyrmions from a topological standpoint, and they form a square lattice[151]. Skyrmions have also been identified recently at room temperature in Pt[Co]/Ir multilayers[158].

The $B-T$ phase diagram of MnSi shown in figure 11.1(b) has been a focus of extensive experimental investigations[11, 28, 29, 159–163] and Monte Carlo simulations[164]. At low temperature and increasing external field, the ordered phases of the system correspond to a helical spin spiral, a conical spin spiral and the collinear field-polarized states. The skyrmion lattice is created from the conical spin spiral state at higher temperature and is
Figure 11.1: Experimentally observed phases in skyrmionic systems. Panel (a) from [23]: spin-polarized scanning tunnelling microscopy measurements performed for Pd/Fe bilayer on Ir(111) at $T = 8$ K, displaying (E) the cycloidal spin spiral, (F) the skyrmion lattice and (G) the field-polarized phases. Colour denotes the out-of-plane component of the spins. Panel (b) from [28]: phase diagram of MnSi inferred from ac susceptibility and specific heat measurements. Displayed are the helical and conical spin spiral phases, the skyrmion lattice phase, as well as the fluctuation-disordered (FD), field-polarized (FP) and paramagnetic (PM) regimes. Solid and scattered lines denote phase transitions and crossovers, respectively.

stable in a small pocket of the $B-T$ phase diagram, where the axis of the skyrmion tubes is aligned parallel to the direction of the external magnetic field $B$. A further peculiarity of the system concerns the transition from the noncollinear spin spiral and skyrmion lattice states into the paramagnetic phase. Above the critical temperature $T_c \approx 29$ K, which value only depends weakly on the external magnetic field, there is a narrow (1-2 K) transition region, which shows critical fluctuations based on neutron scattering[165, 166], susceptibility and specific heat measurements[28, 159, 160, 167] - see figures 11.2(d)-(e). This transition region has generated widespread discussion; earlier papers[166, 168, 169] explained it by the appearance of stable skyrmions in the system even at zero external field; however, these skyrmions do not show long-range order as evidenced by the neutron scattering experiments. On the other hand, the theoretical description in [28, 29, 164] identifies this behaviour with a fluctuation-induced first-order phase transition originally proposed by Brazovskii[170], where the fluctuations are isotropically strong on a surface of a sphere in momentum space.

By comparison, the phases of Pd/Fe/Ir(111) shown in figure 11.1(a) have mainly been investigated at very low temperature in experiments[23, 24]. Similarly, theoretical studies[25, 26, 171] have been only concerned with determining the parameters of a spin model Hamiltonian and the ground state of the system as a function of the external field $B$. In this case, the external field is applied perpendicularly to the surface of the monolayer, leading to the appearance of localized two-dimensional skyrmions. In contrast to MnSi, the skyrmion lattice phase is energetically the most favourable state in a range of external magnetic field values at zero temperature, while the conical spiral state is absent. Without external magnetic field, the ground state is a cycloidal spin spiral state, and at high field values once again the field-polarized state may be observed. Previous theoretical
Figure 11.2: Thermodynamic quantities measured in the different phases of MnSi. Panels (a) and (b) from [11]: small-angle neutron scattering image of (a) the spin spiral ($T = 27\, \text{K}, B = 0\, \text{T}$) and (b) the skyrmion lattice ($T = 26.45\, \text{K}, B = 0.164\, \text{T}$) phases. The multiple pairs of peaks in the spin spiral phase appear as a consequence of the domain structure. Panels (c), (d) and (e) from [29]: small-angle neutron scattering image of (c) the spin spiral phase and (d) the fluctuation-disordered regime ($B = 0\, \text{T}$). (e) Static susceptibility measurement indicating the fluctuation-induced first-order phase transition from the spin spiral phase to the paramagnetic phase. The region between $T_c$ and $T^*$ corresponds to the fluctuation-disordered regime. Solid line was calculated from Brazovskii theory.

Calculations[22, 105, 172] and Monte Carlo simulations[153, 173, 174] performed for model systems confirm the existence of these three types of ordered phases.

In this chapter we will focus on determining the magnetic $B-T$ phase diagram of Pd/Fe/Ir(111) based on the methods discussed in section 7.3. The ab initio calculation of the coupling coefficients was performed in [26]; they will be used as input parameters of the simulations. At the transition from the noncollinear ordered phases to the paramagnetic phase, we identify a strongly fluctuating region, which is much wider than in MnSi. Within the applied model Hamiltonian, the time-dependent fluctuations in this region can clearly be observed. At zero external magnetic field, this corresponds to the formation of such a spin spiral state where the wavelength of the spiral is constant, but the direction of the wave vector is continuously rotating on a circle, in agreement with the description of Brazovskii[170]. At larger magnetic fields, we show that the fluctuations correspond to the creation and annihilation of skyrmions, and determine the lifetime of skyrmions. We note that the skyrmion lifetime in the same system has also been investigated in [27]; however, it focused on the transition from the skyrmion lattice phase to the field-polarized phase instead of the fluctuation-disordered state.

11.1 Ground state properties

For the atomistic simulations we used the spin model (3.1) with the ab initio parameters determined in the paper [26]. We note that the coupling coefficients were calculated by spin cluster expansion in the paramagnetic state[55], rather than the method described in section 2.6 relying on ferromagnetic configurations.

As it was mentioned in section 6.4, the system is ordered in the cycloidal spin spiral
(SS), the hexagonal skyrmion lattice (SkL) or the collinear field-polarized (FP) state at zero temperature, depending on the magnitude of the magnetic field \( B \) applied perpendicularly to the monolayer. This is illustrated in figure 11.3. The energy was determined by finding the equilibrium state with spin dynamics calculations, after initializing the system in a configuration that closely resembles the stable state, such as a harmonic spin spiral (6.1) in the case of the cycloidal spin spiral phase. Since the system has multiple metastable states, the simulations converged to the nearest energy minimum, and the energy values could be compared over a wide range of \( B \) values.

As the spin spiral state has zero net magnetization in the absence of external field, its energy only weakly depends on \( B \), similarly to a paramagnetic system. The energy gain of the field-polarized state is linear in the external field, since all the spins are parallel to the field direction. The skyrmion lattice state has a finite magnetization even without the external field, which magnetization value increases with \( B \) - this will correspond to the ground state of the system for intermediate field values. The obtained upper and lower boundaries of the skyrmion lattice state, \( 1.4 \text{ T} \lesssim B \lesssim 3 \text{ T} \), show good quantitative agreement with the experiments[24]; however, we note that the energies of different states are not explicitly comparable under experimental conditions, and different ordered phases may coexist at the same value of the external magnetic field. The diameter \( d_0 \) of the circle around the skyrmion where the spins lie in the plane changes from approximately 3nm at \( B = 1.4 \text{ T} \) to 2nm at \( B = 3 \text{ T} \) in [24], while in our simulations it changed from 5.1nm to 3.5nm at the same field values.

11.2 Finite-temperature phase diagram

We performed Monte Carlo simulations on an \( N = 128 \times 128 \) lattice at finite temperature, and characterized the different phases in the \( B - T \) plane by the average topological
Figure 11.4: (a)-(b) Average topological number $Q$ in the system as a function of the external field and temperature, calculated from Monte Carlo simulations at a fixed magnetic field for (a) increasing and (b) decreasing temperature. Below $T_c \approx 100$ K, the topological charge did not change during the simulation interval. (c) Phase diagram constructed from the inflection points of the magnetic susceptibility, the line where the fluctuations of the system are frozen and the calculated ground states at zero temperature. Solid lines denote first-order transitions, while staggered lines denote crossovers – see figure 11.1(b). The shallow $FP \rightarrow SkL$ and $SS \rightarrow SkL$ regions between the ordered spin spiral, skyrmion lattice and field-polarized phases denote transitions which could not be resolved by the simulations. The averaging was performed over a simulation length of $10^6$ steps after a thermalization of $2 \times 10^5$ steps.
charge $Q$ (6.14), the static structure factor $S(k)$ (7.6) and the static magnetic susceptibility $\chi$ (7.9). The results obtained for $Q$ are summarized in figures 11.4(a)-(b). The topological charge is only finite in the skyrmion lattice phase out of the three ordered phases. It is apparent that the number of skyrmions in the system is constant below $T_c \approx 100\, \text{K}$, but depends on the direction of the temperature sweep as shown in the differences between figures 11.4 (a) and (b). This hysteresis effect is connected to the finite-sized lattice and the boundary conditions, discussed in detail in appendix B.6. $T_c$ takes an approximately constant value as a function of $B$; although this is in part due to the resolution of the simulations in the $B-T$ space, experiments performed on different systems\cite{11, 28, 156, 159, 160, 163} obtained transition lines with similarly large slopes for $B(T_c)$. As the temperature is increased at a field value corresponding to the skyrmion lattice, the topological charge starts fluctuating above $T_c$ during the simulations, while the average skyrmion number remains the same. This indicates a transition into a fluctuation-disordered (FD) regime\cite{28, 29, 164}, where the skyrmion lifetime is finite. The average topological charge gradually approaches zero as the paramagnetic (PM) regime or the time-reversal-invariant $B = 0\, \text{T}$ line is approached from the direction of the fluctuation-disordered state. However, for sufficiently large external magnetic field ($B \gtrsim 1\, \text{T}$) and low temperature, the topological charge may be basically identified with the number of downwards pointing skyrmions in the system – see the energetical arguments presented in section 6.4. It should be noted that the crossover between the field-polarized and paramagnetic regimes for $B \gtrsim 5\, \text{T}$ is also indicated in figures 10.3(a)-(b) by an increased number of skyrmions.

The identified states are depicted in real and reciprocal space in figure 11.5. The $S(k)$ images are in good agreement with earlier calculations\cite{164, 175} and neutron scattering experiments\cite{11, 29, 152, 156, 165, 166, 176} in figures 11.2(a)-(d). At finite magnetic fields, there is always a peak at $k = 0$, reflecting the finite magnetization of the system. Other than that, the spin spiral phase (figures 11.5(a),(f)) is characterized by two peaks, describing ordering with a single wave vector $k_0$. In the skyrmion lattice state (figures 11.5(b),(g)), there are six extra peaks corresponding to the hexagonal lattice structure. Higher harmonics are also visible in these two phases since neither the spin spiral nor the skyrmion lattice represents a perfect sinusoidal modulation, see \cite{156, 176, 177} and the discussion in section 6.3. The field-polarized regime (figures 11.5(c),(h)) shows no specific features beyond the sharp peak corresponding to the finite magnetization. In the fluctuation-disordered regime (figures 11.5(d),(i)), the central peak of $S(k)$ is surrounded by a circle, while the real-space image shows skyrmion-like spin configurations with topological charge $Q = -1$ and similar radii. Finally, the central peak is surrounded by a Lorentzian curve in the paramagnetic regime (figures 11.5(e),(j)).

The neutron scattering profile in the fluctuation-disordered regime, figure 11.5(i), necessitates some further discussion. It is clearly distinguishable from the paramagnetic regime, where the $S(k)$ curve decreases monotonically with the magnitude of the wave vector. The circle with increased intensity corresponds to a clearly identifiable lengthscale of the magnetic structure, which is absent in the paramagnetic regime. However, the neutron scattering image alone may also indicate the presence of stable skyrmions with infinite lifetime, which show no long-range order either due to their thermal motion as in a skyrmion liquid\cite{178} or their random arrangement as in an amorphous solid\cite{168}. We indeed identified the same profile below $T_c$ in some parts of the skyrmion lattice phase, but this is probably due to the reduced dimensionality of the system, as an amorphous real-space arrangement of skyrmions was also identified experimentally in thin films\cite{23, 153}. \[101\]
Figure 11.5: Spin configurations of the different states in (a)-(e) real space and (g)-(j) reciprocal space $(S(k)$ on logarithmic scale). In the real space figures, red and blue colours denote positive and negative out-of-plane components, respectively. Shown are (a),(g) the spin spiral $(B = 0.6 \; \text{T}, T = 15 \; \text{K})$, (b),(h) the skyrmion lattice $(B = 2 \; \text{T}, T = 15 \; \text{K})$, (c),(i) the field-polarized $(B = 3.2 \; \text{T}, T = 15 \; \text{K})$, (d),(j) the fluctuation-disordered $(B = 2 \; \text{T}, T = 120 \; \text{K})$ and (e),(j) the paramagnetic states $(B = 2 \; \text{T}, T = 310 \; \text{K})$. Compare with the experimental results in figures 11.1(a) and 11.2(a)-(d).
Figure 11.6: Static magnetic susceptibility $\chi$ as a function of temperature for $B = 0$ T. Horizontal lines denote the boundaries of the fluctuation-disordered regime, corresponding to a singularity (solid line) and an inflection point (staggered line) in $\chi$. Compare with the experimental results in figure 11.2.

Figure 11.5(i) may also correspond to an amorphous spin spiral state, where the length of the wave vector of the spiral is fixed, but the direction changes along the lattice, since spin spirals with wave vectors on a circle are almost degenerate in energy. In conclusion, this means that figure 11.5(i) in itself is insufficient for the characterization of the fluctuation-disordered regime. However, also taking into account the real-space images, the fact that the topological charge $Q$ was fluctuating during the simulations, and the specific shape of the susceptibility curve in figure 11.6, it is clear that the fluctuation-disordered regime differs from an amorphous arrangement of magnetic configurations with infinite lifetime. In this regime, the strong fluctuations lead to the creation and destruction of skyrmions on very short timescales. We also note that in [168], the amorphous skyrmion state at $B = 0$ T was explained within a model that accounts for longitudinal spin fluctuations close to the critical temperature; in the Heisenberg model with fixed length of the moments, we only identified the spin spiral, fluctuation-disordered and paramagnetic states for zero external field.

In this system, the static magnetic susceptibility exhibits a finite jump or fall at a first-order phase transition, while crossover points correspond to inflection points in $\chi$ as a function of temperature or magnetic field. The susceptibility at $B = 0$ T is shown in figure 11.6, displaying a remarkable similarity to the curve calculated from the Brazovskii model in figure 11.2(e)[29]. The mentioned model also emphasizes the role of strong fluctuations in driving the transition into the spin spiral state first order. The temperature interval between the jump at the first order transition and the inflection point in the susceptibility may be identified with the fluctuation-disordered state discussed above.

The results of the simulations are summarized in the form of a $B - T$ phase diagram.
in figure 11.4(c). The first-order phase transitions, denoted by solid lines, could be identified by calculating the topological charge $Q$ of the system. $Q$ is zero in the spin spiral and field-polarized phases, which do not meet at any point in the phase diagram; it is finite in both the skyrmion lattice and the fluctuation-disordered phases, but it was changing during the simulations in the latter one. The staggered lines between the field-polarized, fluctuation-disordered and paramagnetic regimes denote crossovers. The transition between these three regimes happens continuously over wide regions, and consequently they are not always identified as distinct thermodynamic phases. The most reliable way to identify the crossover lines in the simulations is finding the inflection points of the $\chi (T)$ and $\chi (B)$ curves, respectively[160]. This was performed by fitting a polynomial on the curves. However, we note that due to the continuous nature of the crossover, the detailed comparison of several different thermodynamic quantities should improve the accuracy of the transition lines as was demonstrated in [160, 162] for MnSi.

We mention that the fluctuation-disordered region in this system is significantly wider ($\approx 150$ K) than in MnSi (1-2 K). A similarly wide transition region has been identified in MnGe at $B = 0$ T[179, 180], though the given interpretation was different. The inflection point of $\chi (T)$ between the field-polarized and the paramagnetic regimes falls in the region with the increased number of skyrmions at large magnetic field in figures 11.4(a)-(b), indicating that the fluctuations also play an important role in this region, but they cannot drive the transition first-order.

Finally, we discuss the intermediate regions SS→SkL and FP→SkL in figure 11.4(c). These do not correspond to actual phases, just denote that the phase transition lines are located within these regions. When performing temperature sweeps as shown in figure 11.4(a)-(b), this is indicated by the fact that the range of magnetic field with high skyrmion number is wider when decreasing the temperature (figure 11.4(b), $1 \ T \lesssim B \lesssim 4$ T) than when increasing the temperature (figure 11.4(a), $1.4 \ T \lesssim B \lesssim 3$ T). This means that for a fixed value of the external field, the skyrmion lattice becomes more favourable at higher temperature compared to either the spin spiral or the field-polarized state. This observation is in agreement with a simple Clausius–Clapeyron model of the phase boundary[28],

$$ \frac{dT}{dB} = -\frac{\Delta M}{\Delta S}. $$

(11.1)

It is known that the skyrmion lattice state has higher entropy than either the spin spiral or the field-polarized state; this is why it is stabilized in MnSi at finite temperature[11, 28]. Therefore, the slope of the transition curve is determined by the magnetization, which increases by going from the spin spiral through the skyrmion lattice to the field-polarized state. This leads to a positive slope of the transition line between the field-polarized and the skyrmion lattice states and a negative slope between the skyrmion lattice and the spin spiral states, in agreement with our previous assumption. The phase transition line between the field-polarized and the skyrmion lattice state in the same Pt/Fe/Ir(111) system as in our calculations is extensively studied in [27], where similarly a positive slope is found and explained using arguments based on the entropy of the system. The experiments and simulations performed on GaV$_4$S$_8$ in [156] obtained the same signs for the slopes as in our model, but both transition lines have a negative slope for Fe$_{0.5}$Co$_{0.5}$Si thin layers as reported in [153]. Unfortunately, we cannot determine these lines of first-order phase transitions from the simulations due to the metastability of all considered ordered states; the obtained phase will always strongly depend on the path taken in the
Figure 11.7: Calculated skyrmion lifetime $\tau_{sk}$ as a function of temperature, implying a good agreement with the Arrhenius law (11.2). The simulations were performed at $B = 2$ T with a Gilbert damping constant $\alpha = 0.05$. The fitted value of the energy barrier is $\Delta E/k_B \approx 2200$ K.

$B - T$ space[164]. We also experienced this effect when the magnetic field was swept at a given temperature. Note that this uncertainty due to metastability also appears under experimental conditions during field-cooling[23, 152, 159, 181, 182].

11.3 Skyrmion lifetime in the fluctuation-disordered regime

Close to the phase boundary between the skyrmion lattice state and the fluctuation-disordered regime, the topological charge takes the same value on the two sides of the boundary, but it can only be calculated as an average in the fluctuation-disordered regime, while it is a constant in the skyrmion lattice state. Therefore, we described this transition by calculating the skyrmion lifetime $\tau_{sk}$ from spin dynamics simulations – the details of the algorithm are given in appendix D.5. The simulations were performed at $B = 2$ T as a function of temperature.

The lifetime of metastable states in magnetic systems quite often follows the Arrhenius law as a function of temperature,

$$\tau_{sk} = \tau_0 e^{\Delta E/(k_BT)}.$$  \hspace{1cm} (11.2)

This expression may also be analytically obtained in some simple cases, one of which is discussed in appendix C.2. As shown in figure 11.7, (11.2) also provides a good description of the skyrmion lifetime, in agreement with earlier works[27, 181, 183, 184]. In our model, the skyrmions in the fluctuation-disordered region are metastable in the sense that they have a finite lifetime because of their finite size, but the system in this region contains a
finite number of skyrmions in the equilibrium, meaning that they are not necessarily ener-
getically unfavourable. Actually, the system forms a skyrmion lattice ground state at this
value of the external field. This must be contrasted with the papers [27, 181, 183, 184],
where the presence of skyrmions is energetically unfavourable with respect to the spin
spiral state or the field-polarized state. We also note that the skyrmion lifetime calculated
in an ensemble of skyrmions in the fluctuation-disordered regime includes processes
which are absent when individual metastable skyrmions are considered on a ferromag-
netic background [27, 183]. For example, skyrmions in the fluctuation-disordered regime
may merge or split, while this effect is obviously absent for individual skyrmions. The
merging effect has already been identified in the three-dimensional system FeCoSi[182] as
the microscopic mechanism behind the transition between the skyrmion lattice and the
helical spin spiral state as the magnetic field is decreased.

For the energy barrier between a skyrmion and a spin configuration without topo-
logical charge, we obtained $\Delta E/k_B \approx 2200$ K. The scalar Heisenberg exchange interaction
between the nearest neighbours, which is by far the strongest interaction between the
spins, is $|J_1|/k_B \approx 400$ K [26]. The skyrmion is unwound if the downwards pointing spin
in the middle of the skyrmion is rotated in the direction parallel to the external field,
during which rotation it loses the exchange energy stabilizing it with respect to its near-
est neighbours, which are almost parallel to it in the initial state. This energy difference
equals approximately $\Delta E \approx 6|J_1|$ – there are six nearest neighbours in the triangular
lattice –, which is close to the value determined from the simulations. This is in agree-
ment with the results in [27] for the same Pd/Fe/Ir(111) system, where an energy barrier
of $\Delta E = 4.7-7.4|J_1|$ was obtained. The different values come from the dependence of
the energy barrier on the applied external magnetic field; we performed the simulations
for a fixed value of $B$. Although in bulk systems skyrmions correspond to lines along
the direction of the external field, they are unwound as a consequence of the appearance
of local defects called monopoles [182], and an energy barrier of $\Delta E \approx 5.8|J_1|$ was re-
ported in [184] for simulations performed on a simple cubic lattice, which contains the
same number of nearest neighbours as the triangular lattice considered here. Experimen-
tally, reference [181] reports $\Delta E/k_B \approx 2000$ K for MnSi, where the exchange interactions
are probably weaker than in Pd/Fe/Ir(111), indicated by the lower critical temperature
$T_c \approx 29$ K. Finally, we mention that in the simulations performed on a square lattice
in [183], the authors obtained $\Delta E \approx 2|J_1|$, in agreement with their theoretical approxi-
mation, which only took into account a single triangle of spins in the energetical and
topological considerations.

In our simulations, the value $T_c \approx 100$ K means that the skyrmion number does not fluctuate below this temperature under the timescale accessible with spin dynamics simu-
lations, $t \approx 100$ ns – see figure 11.7, or for similar equivalent timescales available in Monte
Carlo simulations. If (11.2) holds over a much wider range of temperature, by extrapol-
ation we can obtain that the skyrmion lifetime reaches the 1 s scale around $T_c \approx 50$ K.
Fluctuations on this timescale are accessible to experimental methods as has been demon-
strated in [23, 27, 181], and the experimentally determined critical temperature may be
closer to this value. The skyrmion lifetime in the same system was determined to equal
1 year around 19 K at $B \approx 3$ T in [27], while in our simulations the same value is reached
around 40 K at $B = 2$ T. The difference between the two values may be explained by the fact
that the skyrmion lifetime increases as the external field is decreased as it was demon-
strated in [27]; the significantly smaller value of the determined exchange coefficient in
[27] ($|J_1|/k_B \approx 80$ K); and finally by the fact that both values were obtained by extrap-
olating the Arrhenius law (11.2) from simulation results performed in the nanosecond range, which increases the numerical errors. However, the two theoretical calculations agree in predicting that skyrmions are completely stable against thermal fluctuations at $T = 4.2\,\text{K}$, in agreement with the experiment[23] where skyrmions were generated by current injection in the same material. As a comparison, the ordering temperature reported for the similar system Fe/Ir(111) in [185] is $T_c \approx 28\,\text{K}$. Although this is lower even than the extrapolated value of $T'_c \approx 50\,\text{K}$, it is known from ab initio calculations[25, 26] that the exchange interactions determining the ordering temperature are significantly weaker in the absence of the Pd overlayer.
Chapter 12

Co chain on Au(001): finite-temperature behaviour and switching times

For the future application of magnetic devices on the nanometre scale, it is necessary to understand the magnetism of systems in even lower dimensions than that of ultrathin films. In particular, finite and infinite chains of magnetic atoms have been widely discussed in the literature. In a biatomic chain of Fe atoms on Ir(001), a short-wavelength spin spiral state have been observed using spin-polarized scanning tunnelling microscopy experiments\([186]\), the chirality of which is determined by the Dzyaloshinsky–Moriya interaction. \textit{Ab initio} calculations revealed that a chain of Mn atoms on Ni(001) surface may also form a noncollinear magnetic ground state depending on the parity of atoms in the chain\([187]\). Finally, it was shown in \([188]\) using model calculations that metastable noncollinear spin configurations may also be used to store energy.

As was demonstrated in \([31]\) and shown in figure 12.1, monatomic Co chains located in the step edges of Pt(997) surface order ferromagnetically with a canted easy axis direction with respect to the main crystallographic axes of bulk Pt. Naturally, this ordering only pertains to a finite chain within a finite experimental investigation timescale; even the Ising model, corresponding to infinitely strong anisotropy, shows no long-range order in one dimension at finite temperature\([30]\). This discovery motivated further experimental and theoretical investigations of the system\([189–191]\). In \([192]\), the magnetic ground state was determined by applying the embedded Korringa–Kohn–Rostoker cluster method to the chain and minimizing the energy within constrained density functional theory\([46, 193, 194]\); it was concluded that the ground state is not perfectly collinear due to relativistic effects.

According to \textit{ab initio} calculations, infinite Co chains also order ferromagnetically at zero temperature, both when they are free-standing\([195–198]\) and when they are located on the surface of bulk Cu or Pt\([199, 200]\). In comparison, the ground state of unsupported V, Mn and Fe chains is noncollinear\([197, 198]\). Considering relativistic effects, it was found in \([200]\) that the easy axis is perpendicular to the chain in the free-standing case and parallel to it when the atoms are located on the (001) surface of Cu. However, finite-temperature effects were generally not included in the calculations; in \([198]\), the electronic temperature was taken into account, but nevertheless an energy minimization procedure was performed.

In this chapter, we will test the speed and stability of the numerical solvers of the
stochastic Landau–Lifshitz–Gilbert equation written in the local coordinate system, which were introduced in section 5.4. After finding the most suitable method for the \textit{ab initio} cluster spin dynamics simulations described in section 7.2, we will apply it to a linear chain of ten Co atoms on Au(001) surface. Although the ground state is almost ferromagnetic with the easy axis along the chain direction, the Dzyaloshinsky–Moriya interaction induces a small noncollinearity of the spins. We will also construct minimal model Hamiltonians which can reproduce the behaviour of different physical quantities observed at finite temperature. It will be shown that an isotropic nearest-neighbour Heisenberg model is sufficient for describing the temperature dependence of the mean energy and squared magnetization, while adding an on-site anisotropy term is required for understanding the switching processes between the two energetically degenerate magnetization directions parallel to the easy axis.

### 12.1 Testing the numerical integration schemes on the model Hamiltonian

It is advisable to perform the investigation of the numerical integration schemes on an analytically solvable model; this way, the simulation results are comparable to exact values. For this purpose, we considered a linear chain consisting of $N$ spins, where only the nearest neighbours interact with a ferromagnetic scalar Heisenberg coupling $J < 0$. The corresponding model Hamiltonian is

$$H = \sum_{i=1}^{N-1} J S_i S_{i+1}. \quad (12.1)$$
The analytical solution at finite temperature is discussed in [201] and in appendix D.6; here we will only present the expression for the expectation value of the energy and the squared magnetization. The first one has the form

$$\langle E \rangle (T) = - (N - 1) JL \left( \frac{J}{k_B T} \right), \quad (12.2)$$

with

$$L (x) = \coth x - \frac{1}{x} \quad (12.3)$$

the Langevin function. Note that (12.2) is an even function of $J$, meaning that the ferromagnetic and the antiferromagnetic models behave analogously. This does not hold for the quantum case[202], where determining the correct ground state of the antiferromagnetic system is a complicated problem in and of itself[203, 204].

Regarding the magnetization, the expectation value of the spin vector averaged over the chain or calculated at a given lattice site disappears at finite temperature due to the time-reversal invariance of the Hamiltonian (12.1); this remains true for the infinite chain as there is no spontaneous symmetry breaking in the one-dimensional model. Instead we will determine

$$\langle M^2 \rangle (T) = \frac{M^2}{N^2} \sum_{i,j} \langle S_i S_j \rangle, \quad (12.4)$$

which will always take a finite positive value for a finite chain. Here $M$ denotes the size of the magnetic moment. Following the derivation in appendix D.6, (12.4) transforms into

$$\langle M^2 \rangle (T) = \frac{M^2}{N^2} \left( \frac{1 + L \left( \frac{-J}{k_B T} \right)}{1 - L \left( \frac{-J}{k_B T} \right)} - 2L \left( \frac{-J}{k_B T} \right) \frac{1 - L \left( \frac{-J}{k_B T} \right)^N}{\left(1 - L \left( \frac{-J}{k_B T} \right)^N\right)^2} \right). \quad (12.5)$$

The numerical integration schemes presented in section 5.4 were tested on the system defined by (12.1). Since the system is described by a model Hamiltonian, the derivatives in the local coordinate system required during the integrations were calculated by using (2.43)-(2.51) given in section 2.6. Furthermore, it was possible to compare the results to the semi-implicit B method in [86], which is defined in the global coordinate system. The errors of the simulations were approximated by the method described in appendix C.5.

Figure 12.2 demonstrates that all three methods proposed in section 5.4, namely the two-step scheme (5.32), the one-step scheme (5.33) and the simplified one-step scheme (5.34), correctly describe the thermal equilibrium of the system, since the average energy value is very close to the analytical expression (12.2). The global two-step scheme denotes the semi-implicit B method[86]. The next question was that how fast the numerical integrations can be performed, which is mainly determined by the time step of the simulation. It is shown in figure 12.3 that the average energy value calculated from the simulations diverges from the analytical value as the time step $\Delta t$ is increased, indicating that the numerical solver becomes unstable. For the simplified one-step scheme, this divergence happens at an approximately 100 time smaller time step than for the other two methods. Since the main bottleneck during the calculations is the \textit{ab initio} determination of the
Figure 12.2: Statistical average of the energy of the Heisenberg chain as a function of the temperature, obtained using different numerical schemes. The mean value is calculated by running the simulation for 500000 time units $M/\gamma$, and averaging the value of the energy at the last time step over 200 different realizations, corresponding to different seeds of the random number generator. The error bars denote the 95% confidence intervals. The time step was $\Delta t = 0.05 M/\gamma$ for the first three schemes and $\Delta t = 0.001 M/\gamma$ in the case of the simplified one-step scheme. The other simulation parameters are $J = -1, N = 50$ and $\alpha = 0.05$.

Figure 12.3: Statistical average of the energy of the Heisenberg chain as a function of time step, obtained using different numerical schemes. The mean value is calculated by running the simulation for 500000 time units $M/\gamma$, and averaging the value of the energy at the last time step over 200 different realizations, corresponding to different seeds of the random number generator. The error bars denote the 95% confidence intervals. The other simulation parameters are $J = -1, k_B T = 0.1, N = 50$ and $\alpha = 0.05$. 

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Figure 12.4: Illustration of the cluster of ten Co atoms (blue) forming a linear chain on Au(001) surface (gold), along with the ground state spin configuration. Red and blue colours of the spin denote positive and negative out-of-plane components, respectively.

Torques acting on the spins, not the actual numerical integrations, the simplified one-step scheme can be omitted from further considerations. Although the global two-step scheme is the most stable method, it is not written in the local coordinate system, and therefore is unsuitable for the \textit{ab initio} calculations. Finally, the one-step and two-step schemes can be used with basically the same time steps, but the latter requires twice as many \textit{ab initio} calculations, both for the predictor and the corrector parts. Based on these observations, we used the one-step scheme for the numerical integration of the stochastic Landau–Lifshitz–Gilbert equation in the \textit{ab initio} code.

Finally, we mention that the maximal time step is given here in natural $M/\gamma$ units, for exchange interactions of unit strength $J = -1$. In the case of periodic boundary conditions, the spin wave frequencies of the one-dimensional Heisenberg model read

\[
\omega_k = -\frac{\gamma}{M} 2J \left( 1 - \cos \left( 2\pi \frac{k}{N} \right) \right),
\]

for $k = 1, \ldots, N$. The maximal time step must be compared to the period of the spin wave with the highest frequency, $4|J|\gamma/M$. This means that during the \textit{ab initio} calculations, first one has to determine the spin wave frequencies as described in section 3.3, and choose the time step accordingly.

12.2 Equilibrium properties

The \textit{ab initio} spin dynamics simulation method was applied to a chain of ten Co atoms forming a linear chain on Au(001) surface in fcc growth, shown in figure 12.4. We did not consider lattice relaxations in this system, the Co atoms occupied the positions of the bulk Au fcc lattice. The ground state spin configuration and potential was determined self-consistently as discussed in section 7.1.
It is apparent from figure 12.4 that the ground state of the system is close to being ferromagnetic, with the easy axis along the chain direction. The direction of the easy axis is the same as for infinite Co chains on Cu(001) surface[199, 200]. The $xz$ plane going through the chain constitutes a symmetry plane of the system, which implies that the Dzyaloshinsky–Moriya interaction between any two Co atoms must be parallel to the $y$ direction – see section 6.1. As shown in figure 12.4, the Dzyaloshinsky–Moriya interaction slightly tilts the spin out of the $x$ direction towards a right-rotating cycloidal spin spiral in the $xz$ plane. However, this tilting is small even at the ends of the chain, where the atoms with reduced coordination numbers are located. This indicates that the ground state of the infinite chain is probably ferromagnetic due to the anisotropy. This is in agreement with previous studies[197, 198] performed for infinite free-standing Co chains. However, it must be noted that the Dzyaloshinsky–Moriya interaction which could destabilize the ferromagnetic order only appears due to the presence of the substrate; therefore, it was absent in the calculations performed for the free-standing case.

Since the ground state of the system indicates similarity to the simple monatomic Heisenberg chain discussed in section 12.1, we compared the thermal properties of the system to the analytical expressions obtained from the model Hamiltonian. The results are summarized in figure 12.5. For the energy, we used (12.2) with the exchange interaction as the fitting parameter, and obtained a value of $J = -3.64 \pm 0.24\text{mRy}$. The exchange interaction may also be determined by fitting the torque values calculated from ab initio methods to a model Hamiltonian – see section 2.6. Only considering scalar Heisenberg coupling (2.39), we obtained values between $-3.16$ and $-4.47\text{mRy}$ for the nearest neighbours, being enhanced at the ends of the cluster. The average value of $-3.58\text{mRy}$ is in good agreement with the fitted value from the simple analytical model, indicating that if one is only interested in the energy of the system, the isotropic Heisenberg chain provides a good description. We note that the determined exchange interactions are significantly weaker than in the case of the free-standing chain, $-11.5\text{mRy}$ in [197] and $-13\text{mRy}$ at $T = 0$ electronic temperature in [198]. This is mostly explained by the fact that the Co atoms are located closer to each other in the free-standing chain than when they are confined to the fcc lattice with the lattice constant of Au. The interactions between the next-nearest neighbours are ferromagnetic, but about ten times weaker than for the nearest neighbours, while between the third-nearest neighbours an antiferromagnetic coupling was found. These observations are in good agreement with previous calculations[197, 198].

The average magnetization of the cluster in figure 12.5(b) was obtained from the squared magnetization, $M_{avg} = \sqrt{\langle M^2 \rangle}$ with $M$ from (7.1). The mean values of the simulations were fitted to the analytical expression (12.5), with the magnetic moment $M$ as the only fitting parameter, since $J$ was already determined from the temperature dependence of the energy. From the fit we obtained $M = 1.694 \pm 0.006 \mu_B$, while the ab initio calculations using (2.31) yielded magnetic moments between $1.656 \mu_B$ and $1.689 \mu_B$, with the average value of $1.670 \mu_B$. This result lends further credence to the applicability of the nearest-neighbour Heisenberg model for the present system.

### 12.3 Switching properties

In order to go beyond the isotropic Heisenberg model, we have to calculate a different quantity. Due to the easy axis along the $x$ direction and the time-reversal invariance of
Figure 12.5: Average (a) energy $E$ and (b) magnetization $M_{\text{avg}} = \sqrt{\langle M^2 \rangle}$ as a function of temperature for the monatomic Co chain. The mean values are calculated by running the simulations for 50000 time units $t_0 = \frac{\hbar}{2\text{Ry}} = 24.2$ as, and taking the average at the last time step over 50 different realizations, corresponding to different seeds of the random number generator. The error bars denote the 95% confidence intervals. The solid lines denote fits with the analytical expressions for the finite Heisenberg chain, (12.2) and (12.5) for the energy and the magnetization, respectively. The time step $\Delta t = 5t_0$ was determined by calculating the normal modes of the system as discussed in section 3.3, yielding a maximal frequency of $\omega_{\text{max}} = 8.27t_0^{-1}$. The value of the damping parameter was $\alpha = 0.05$. 

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the system, at finite temperature the chain will be constantly switching magnetization between the positive and negative $x$ directions. It is expected that such a switching process gives information about the anisotropy, as this is the quantity that determines the energy barrier between the two states.

During the switching process illustrated in figure 12.6, the system gets relatively far from the ground state. At each time step, we compared the exchange-correlation field directions $\{e_i\}$ (2.16) to the orientation of the calculated spin magnetic moments $\{M^\text{spin}_i\}$ (2.31), and found that the angle between them was never larger than $3^\circ$. Moreover, the magnitudes of $M^\text{spin}_i$ fluctuated within just a $\pm 2\%$ wide range around the corresponding ground state value, occasionally reaching values up to $\pm 5\%$. This indicates that identifying the spin vectors $S_i$ with the direction of the exchange-correlation field $e_i$ instead of the direction of the magnetic moment $M^\text{spin}_i$ is a justified assumption for stable magnetic moments.

The switching time was calculated by starting the simulations with all spins along the positive $x$ direction, and determining the first time instance where $M^x < -1.0 \mu_B$. With an average spin magnetic moment of $1.670 \mu_B$, this threshold value is sufficiently close to the other energy minimum with spins along the negative $x$ direction.

The results of the $ab\ initio$ simulations are summarized in figure 12.7. The expectation value $E^x(\tau)$ of the switching time $\tau$ follows

$$E^x(\tau) = \tau_0 e^{\Delta E/\kappa},$$

the well-known Arrhenius expression for crossing temperature barriers. Since (12.7) was first derived by Néel[205] for magnetic particles, in this context it is also known as the Arrhenius–Néel law. The derivation of (12.7) for a single spin is given in appendix C.2,
and we also supposed a similar temperature dependence for the skyrmion lifetime (11.2) in section 11.3.

Note that we calculated the median value of the switching times $\tau_{\text{median}}$ instead of the mean value, which would approximate the expectation value $E^x(\tau)$. Calculating $\tau_{\text{median}}$ instead of the average of the switching times is computationally less demanding: one has to take the middle value of the flipping times, so the maximal simulation time corresponds to the time interval for which half of the realizations displays a flipping. If we assume that the switching time $\tau$ follows exponential distribution, the simple proportionality $\tau_{\text{median}}/\ln 2 = E^x (\tau)$ holds; therefore, $\tau_{\text{median}}$ should also follow (12.7) with the same energy barrier $\Delta E$, but a different prefactor $\tau_0$.

Once again, we constructed a simple spin Hamiltonian which could quantitatively reproduce the observed switching behaviour, along with the thermal properties discussed above. For this purpose, we added an easy-axis on-site anisotropy parameter $K^{xx} < 0$ to the isotropic Heisenberg model (12.1). The switching time of such a model Hamiltonian is examined in detail in [206], and it is shown that the energy barrier $\Delta E$ strongly depends on the length of the chain compared to the domain wall width $L_{\text{DW}} = 2\sqrt{J/K^{xx}}$. For very short chains, the spins rotate collectively at low temperature, and the energy barrier is determined by the anisotropy $K^{xx}$ as in the case of a single magnetic particle. For long chains, the switching happens as a domain wall is formed at one end, and this wall propagates along the chain until the other end. This scenario is similar to the behaviour of an Ising model, and the switching time and propagation velocity is determined by the exchange interaction $J$.

Therefore, we used the model parameters $J = -3.6 \, \text{mRy}$ and $M = 1.67 \, \mu_B$ determined from the thermal equilibrium properties, and performed the simulations for different values of $K^{xx}$. As shown in table 12.1, the value $K^{xx} = -0.24 \, \text{mRy}$ can reproduce...
the energy barrier $\Delta E$ and the prefactor $\tau_0$ within the error of the fitting parameters. Calculating the band energy of the system in ferromagnetic configurations along different crystallographic axes yields the anisotropy energies $(E_x^z - E_y^z)/N = -0.26\text{mRy}$ and $(E_x^z - E_y^z)/N = -0.17\text{mRy}$, which are comparable to the value determined above. We mention that $K^{zx} = -0.09\text{mRy}$ was obtained for an infinite Co chain on Cu(001) in [199]. Regarding the model calculations in [206] discussed above, the domain wall width $L_{\text{DW}} = 7.75$ in the system is comparable to the chain length $N = 10$. Therefore, switching processes may occur both as collective rotations and due to the creation of domain walls; for an example of the latter case see figure 12.6, where the fluctuations between 12\,ps and 18\,ps correspond to the Brownian motion of the domain wall.

<table>
<thead>
<tr>
<th></th>
<th>$\ln(\tau_0/t_0)$</th>
<th>$\Delta E/k_B$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ab initio</td>
<td>11.30±0.24</td>
<td>224±17</td>
</tr>
<tr>
<td>model</td>
<td>11.26±0.18</td>
<td>230±13</td>
</tr>
</tbody>
</table>

Table 12.1: The parameters of the Arrhenius law fit to the $\tau_{\text{median}}$ values obtained from the ab initio and model simulations as a function of temperature, see figure 12.7. The parameters of the model Hamiltonian are $J = -3.6\text{mRy}$ and $K^{zx} = -0.24\text{mRy}$. The time unit is $t_0 = \frac{\hbar}{2\text{mRy}} = 24.2\text{as}$. 
Chapter 13

Conclusion and thesis statements

In this thesis we have combined ab initio electronic structure theory with classical atomistic spin dynamics and Monte Carlo simulations for analysing the magnetic properties of ultrathin films and nanoclusters. We have also presented some simple but powerful theoretical methods, which are capable of providing a qualitatively – in some cases, also quantitatively – correct description of the systems. The explained effects include equilibrium properties such as magnetic phases and phase transitions, as well as the dynamical behaviour encapsulated in spin wave excitations and switching times.

The screened Korringa–Kohn–Rostoker method based on density functional theory was primarily applied to systems consisting of transition metals. However, we have demonstrated that these materials with relatively simple lattice structure display a wide array of magnetic phenomena, ranging from noncollinear ordered phases, through spin waves reflecting the chirality of the system, to localized spin configurations with finite lifetime. Expanding the method to deal with more complicated systems seems promising for opening new research directions.

The calculation of spin waves around an arbitrary equilibrium state and its extension to finite temperature using perturbative methods provides a way of characterizing different systems, basically without restrictions on the dimensionality or the lattice structure. Despite its simplicity, mean-field theory is also applicable for describing all types of phase transitions beyond the well-known ferromagnetic-paramagnetic transition.

We have also presented the theoretical background behind the numerical solution of the stochastic Landau–Lifshitz–Gilbert equation, which may help in constructing correct stochastic descriptions for macrospin models at finite temperature.

Overall, we hope that the methods summarized in this thesis contribute to a better understanding of magnetism, possibly even beyond the system-specific results.

Thesis statements

Each of my thesis statements corresponds to the summary of one of the results chapters 8-12. They are sorted by their order of appearance in the manuscript.

1. I have determined the linear response function of a magnetic monolayer to an external time-dependent magnetic field using spin dynamics simulations. I have demonstrated that thermal fluctuations decrease the spin wave frequencies, and that this phenomenon can be quantitatively explained by perturbation theory based on spin waves. The results are published in paper [1].

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2. I have determined the interaction coefficients and ground states in Fe mono- and double-layers on W(110). The in-plane ferromagnetic phase of the monolayer is in agreement with the experiments. Although the \textit{ab initio} calculations could not reproduce the spin spiral ground state of the double-layer, Monte Carlo simulations confirmed the observed reorientation of the easy axis from out-of-plane to in-plane as the temperature is increased. I have demonstrated possible phase transitions between a spin spiral phase and the ferromagnetic phase magnetized perpendicularly to the spiral plane as a function of temperature using mean-field theory and Monte Carlo simulations. I have predicted the presence of an elliptic conical spin spiral state in Fe double-layer on W(110), which has not been observed experimentally so far. The results are partially published in papers [III] and [IV].

3. I have determined the interaction coefficients and ground states in an Fe monolayer on Ta(110). Depending on the distance between the monolayer and the substrate, I have identified four possible ground states in the system, three of them being noncollinear spin spiral states. I have predicted a transition from the ferromagnetic to the SS I, as well as from the SS II to the SS I state as the temperature is increased, by relying on spin wave expansion and Monte Carlo simulations. I have used mean-field theory to explain the transition from the SS III to the SS II state observed in the simulations. The results are published in paper [IV].

4. I have determined the $B-T$ phase diagram of PdFe bilayer on Ir(111) using Monte Carlo simulations. Besides the long-range ordered cycloidal spin spiral, skyrmion lattice and field-polarized states, I have found an intermediate state displaying short-range order, where the topological charge was fluctuating. Based on the similarity of the calculated static susceptibility and static structure factor to the experimental results for the bulk skyrmionic system MnSi, I have identified this intermediate regime as the fluctuation-disordered state. I have emphasized the importance of finite skyrmion lifetime in this regime at finite external magnetic field, and calculated said lifetime from spin dynamics simulations. The results are published in paper [V].

5. I have constructed three numerical solvers to the stochastic Landau–Lifshitz–Gilbert equation written in the local coordinate system, which I have implemented in the screened Korringa–Kohn–Rostoker code. Based on the stability analysis performed on a simple Heisenberg chain, I have determined that the one-step scheme is the most suitable one for the application in question. Using \textit{ab initio} spin dynamics simulations, I have examined a chain of ten Co atoms on Au(001) surface. Despite a slight canting of the ground state due to the Dzyaloshinsky–Moriya interactions, I have demonstrated that the thermal equilibrium properties may be sufficiently described by a nearest-neighbour Heisenberg model, while including an on-site anisotropy term can explain the observed switching times. The results are published in paper [II].

Publications connected to thesis statements:


Other publications:

Appendix A

Electronic structure theory

A.1 The Hohenberg–Kohn theorem

In the following sections we will derive the Kohn–Sham–Dirac equation (2.2) in section 2.1. For a nonrelativistic electronic system, the Hamiltonian in (2.1) may be written in coordinate representation as

$$ H = \sum_i \frac{p_i^2}{2m} + \sum_i V(\mathbf{r}_i) + \frac{1}{2} \sum_{i \neq j} \frac{k_C e^2}{|\mathbf{r}_i - \mathbf{r}_j|} = T + V + W, \quad (A.1) $$

with \( p_i = -i\hbar \nabla_i \); \( \hbar, k_C, m \) and \( e \) standing for the Planck and Coulomb constants, as well as the mass and charge of the electron, respectively. The Hamiltonian was decomposed into the kinetic energy part \( T \), the potential \( V \) and the Coulomb interaction \( W \). The effect of the atomic nuclei is included in the potential with their positions considered fixed, that is, in a Born–Oppenheimer approximation. The electronic density at point \( \mathbf{r} \) in the state \( \Psi = \Psi (\{ \mathbf{r}_i \}) \) is given by

$$ n(\mathbf{r}) = \int \left| \Psi \left( \mathbf{r}_1 = \mathbf{r}, \{ \mathbf{r}_i \}_{i \neq 1} \right) \right|^2 \prod_{i \neq 1} d^3 \mathbf{r}_i. \quad (A.2) $$

Here \( \Psi = \Psi (\{ \mathbf{r}_i \}) \) is normalized to the number of electrons in the system, \( N \). If the kinetic energy and interaction expressions are fixed, the potential \( V \) obviously determines the ground state energy \( E_0 \) and wave function \( \Psi_0 \), and therefore the density in this ground state \( n_0(\mathbf{r}) \), by the solution of equation (2.1). The first part of the Hohenberg–Kohn theorem[207] states that this relation is invertible in some sense: any ground state density \( n_0(\mathbf{r}) \) which can be obtained from a potential \( V \) determines this potential up to an additive constant. This means that the ground state expectation value of any operator may be expressed as a functional of the density. In particular, for the Hamiltonian one has

$$ \langle \Psi_0 | H | \Psi_0 \rangle = E_0 = F_{\text{HK}} [n_0] + \int n_0(\mathbf{r}) V(\mathbf{r}) d^3 \mathbf{r}, \quad (A.3) $$

where the Hohenberg–Kohn functional \( F_{\text{HK}} [n_0] \) contains the contributions of \( T \) and \( W \) to the ground state energy. Since \( F_{\text{HK}} [n_0] \) does not depend on the potential \( V \), one can fix the function \( V = V_0 \), and construct the energy functional

$$ E_{V_0} [n] = F_{\text{HK}} [n] + \int n(\mathbf{r}) V_0(\mathbf{r}) d^3 \mathbf{r}, \quad (A.4) $$
where \( n \) is the ground state density of some system of the form (A.1), but not necessarily the system with potential \( V_0 \). The second part of the Hohenberg–Kohn theorem states that finding the ground state density \( n_0 \) belonging to \( V_0 \) is possible by minimizing (A.4),

\[
E_0 = E_{V_0} [n_0] = \min_n E_{V_0} [n].
\] (A.5)

Thus the determination of the ground state density may be reformulated as a variational problem. The Hohenberg–Kohn theorem may be extended to degenerate ground states and the minimization in (A.5) to densities \( n \) which are not the ground state density of a system of the form (A.1). For the proof of the theorem and these generalizations the reader is referred to a textbook on density functional theory such as [39].

### A.2 The Kohn–Sham scheme

Unfortunately, the minimization procedure (A.5) cannot be carried out in practice, because the explicit form of the functional \( F_{\text{HK}} \) \( [n] \) is not known. As mentioned in section 2.1, the Kohn–Sham method[42] is based on the assumption that the minimization (A.5), which calculates the ground state density for the potential \( V_0 \), is equivalent to finding the ground state of a noninteracting system with a different potential \( V_s \). For a noninteracting system, one has to solve the single-particle Schrödinger equation

\[
\left( \frac{p^2}{2m} + V_s (r) \right) \psi_n (r) = \varepsilon_n \psi_n (r),
\] (A.6)

which leads to the ground state density

\[
n_0 (r) = \sum_{n=1}^{N} \psi_n^\dagger (r) \psi_n (r),
\] (A.7)

where the sum is performed over the states with the lowest eigenvalues from (A.6), and the number of states equals the number of electrons \( N \) in the system. Equations (A.6)-(A.7) must be solved self-consistently, since \( V_s (r) \) is a function of the density \( n (r) \). The single-particle potential may be obtained from \( V_0 \) through (2.7), with the exchange-correlation potential

\[
V_{\text{xc}} (r) = \frac{\delta E_{\text{xc}}}{\delta n (r)} \bigg|_{n=n_0},
\] (A.8)

\[
E_{\text{xc}} [n] = F_{\text{HK}} [n] - \frac{1}{2} \int \int \frac{k_c \epsilon^2}{|r-r'|} n (r) n (r') d^3r d^3r' - \sum_{n=1}^{N} \int \psi_n^\dagger (r) \frac{p^2}{2m} \psi_n (r) d^3r.
\] (A.9)

The Kohn–Sham theorem states that the ground state density of the system described by equations (A.6)-(A.7) will be the same as the density obtained from the minimization procedure (A.5). This theorem can also be proved rigorously under certain conditions[39].

The main shortcoming of the Kohn–Sham scheme is that the explicit form of \( E_{\text{xc}} [n] \), and therefore \( V_{\text{xc}} (r) \), is still unknown, so the equations cannot be solved exactly. The largest energy contributions to the energy functional \( F_{\text{HK}} [n] \), namely the kinetic energy of the noninteracting fermions and the Hartree approximation of the Coulomb energy, are handled separately from \( E_{\text{xc}} [n] \), but one must still find an approximation for the remaining part.
A.3 The local density approximation

The most widespread method for constructing $E_{xc}[n]$ is the local density approximation, which was also used in our calculations. It is based on the ground state of the homogeneous electron gas where a constant positive background potential is used. Since this system is translationally invariant, the density does not depend on the position vector, $n(r) = n$. Even in this case, finding the ground state energy of the interacting system is a complicated many-body problem, which is widely discussed in the literature. Actually, within the local density approximation there exist multiple possible functional forms of the exchange-correlation energy based on the accuracy of the calculated ground state energy of the homogeneous electron gas; for examples see [39]. If the ground state energy is known, the exchange-correlation energy $E_{xc}^{\text{beg}}[n]$ may be obtained by the definitions (A.3) and (A.9). By introducing the energy density

$$
\epsilon_{xc}^{\text{beg}}(n) = \frac{1}{V} E_{xc}^{\text{beg}}[n],
$$

(A.10)

the local density approximation is based on replacing the density $n$ with the local value $n(r)$ and calculating the exchange-correlation energy as

$$
E_{xc}[n] = \int \epsilon_{xc}^{\text{beg}}(n(r)) d^3r.
$$

(A.11)

A.4 The total energy

The knowledge of a proper approximation for $E_{xc}[n]$ permits the solution of the Kohn–Sham equation (A.6). However, the Kohn–Sham theorem only states that the ground state density of the noninteracting system is the same as the ground state density of the interacting system. The expectation values of other operators are functionals of the ground state density, but the forms of these functionals are not known explicitly, just as it was the case with $E_{xc}[n]$. The ground state total energy of the system is

$$
E_0 = \sum_{n=1}^{N} \varepsilon_n - \frac{1}{2} \int \int \frac{k_F^2 \varepsilon_0^2}{|\mathbf{r} - \mathbf{r}'|} n_0(\mathbf{r}) n_0(\mathbf{r}') d^3\mathbf{r} d^3\mathbf{r}' + E_{xc}[n_0] - \int n_0(\mathbf{r}) V_{xc}(\mathbf{r}),
$$

(A.12)

which can be calculated once $E_{xc}[n]$ is known. For other quantities, one has to generally rely on the noninteracting system (A.6), and treat the $\psi_n$ vectors as eigenvectors and the $\varepsilon_n$ values as energy levels. However, this will not always give accurate results; for example, it is clear from (A.12) that the energy of the interacting system is different from the energy of the noninteracting system, the latter corresponding to the sum of the eigenvalues $\varepsilon_n$. It is also known that the band gap of semiconductors and insulators calculated from the Kohn–Sham scheme is generally significantly smaller than the experimental value. For these systems, the local density approximation must be extended with further corrections to produce accurate results.

In this thesis, we have only treated metallic systems for which the local density approximation with the Kohn–Sham scheme is generally reliable. For example, the Fermi energy may be identified with the highest eigenvalue $\varepsilon_n$ present in the ground state of the system.
A.5 The spin-polarized Kohn–Sham scheme

For the description of magnetic systems it is necessary to incorporate the electron spin into the calculations[208]. In the nonrelativistic Kohn–Sham scheme this is done by introducing two-component spinors, similarly to how the Pauli–Schrödinger equation is constructed from the spinless Schrödinger equation. This leads to

\[
\left( \frac{\mathbf{p}^2}{2m} + V_s (\mathbf{r}) + \mu_B \mathbf{B}_s (\mathbf{r}) \mathbf{\sigma} \right) \psi_n (\mathbf{r}) = \varepsilon_n \psi_n (\mathbf{r}),
\]

(A.13)

where \( \mu_B = \frac{e \hbar}{2m} \) is the Bohr magneton and \( \mathbf{\sigma} \) the vector formed from the Pauli matrices. In this case, the potential \( V_s \) and the magnetic field \( \mathbf{B}_s \) may depend on the magnetization \( \mathbf{m} (\mathbf{r}) \) as well as the electron density \( n (\mathbf{r}) \); for a noninteracting system these are defined as

\[
n (\mathbf{r}) = \sum_{n=1}^N \bar{\psi}_n^\dagger (\mathbf{r}) \psi_n (\mathbf{r}),
\]

(A.14)

\[
\mathbf{m} (\mathbf{r}) = - \mu_B \sum_{n=1}^N \bar{\psi}_n^\dagger (\mathbf{r}) \mathbf{\sigma} \psi_n (\mathbf{r}).
\]

(A.15)

The effective single-particle magnetic field has the form (2.8), with

\[
\mathbf{B}_{xc} (\mathbf{r}) = \frac{\delta E_{xc}}{\delta \mathbf{m} (\mathbf{r})}
\]

(A.16)

the exchange-correlation magnetic field. If the external field is zero, one can identify the \( z \) axis with the direction of \( \mathbf{B}_{xc} (\mathbf{r}) \); it is usually supposed that this direction does not depend on the position \( \mathbf{r} \). In this case, \( \mathbf{m} (\mathbf{r}) \) will be parallel to the \( z \) axis in the ground state, and one can work with the densities of the spin-up and spin-down electrons in this coordinate system,

\[
n (\mathbf{r}) = n_+ (\mathbf{r}) + n_- (\mathbf{r}),
\]

(A.17)

\[
m (\mathbf{r}) = - \mu_B (n_+ (\mathbf{r}) - n_- (\mathbf{r})).
\]

(A.18)

Similarly to the local density approximation, \( E_{xc} [n_+, n_-] \) may be expressed by calculating the exchange-correlation energy for a spin-polarized homogeneous electron gas, and replacing \( n_+ \) and \( n_- \) with their local values.

A.6 The relativistic Kohn–Sham–Dirac scheme

As mentioned in section 2.1, the electronic structure calculations discussed in this thesis were based on the relativistic version of density functional theory[209]. The relativistic theory of electrons may be described within the terms of quantum electrodynamics, which leads to field equations describing the motion of electrons and photons. The electronic density \( n (\mathbf{r}) \) of the nonrelativistic case is replaced by the current \( J^\mu (x) \), which is a four-vector as a function of the four-vector coordinate \( x \). Similarly, the external potential \( V (\mathbf{r}) \) is replaced by the four-vector potential \( A^\mu (\mathbf{r}) \). In its relativistic form, the Kohn–Sham theorem states that for every interacting system, there exists a noninteracting system of
electrons with the same ground state current and a different vector potential $A_s^\mu (r)$. The noninteracting system is described by the Dirac equation

$$(e\alpha (p + eA_s) - eA_s^0 + \beta mc^2) \psi_n = \varepsilon_n \psi_n,$$  

(A.19)

with the definitions (2.3)-(2.5).

The current $J^\mu$ in the noninteracting system may be calculated as

$$J^\mu (x) = -e \sum_n \psi^\dagger (x) \gamma^0 \gamma^\mu \psi (x),$$  

(A.20)

where the sum only goes over the electrons with $\varepsilon_{\text{Fermi}} > \varepsilon_n > mc^2$ if vacuum polarisation effects are ignored. The energy functional of the system is decomposed as

$$E_{A_s^\mu} [J^\mu] = T_s [J^\mu] + \int J^\mu (x) A^\mu (r) d^3r + \frac{1}{2} \int \int \frac{k_c J^\mu (x) J^\mu (x')}{|r - r'|} d^3r d^3r' + E_{\text{xc}},$$  

(A.21)

where $T_s$ is the kinetic energy functional of noninteracting electrons. This leads to the effective single-particle potential

$$A_s^\mu (r) = A^\mu (r) + \int \frac{k_c J^\mu (x')}{|r - r'|} d^3r' + \frac{\delta E_{\text{xc}}}{\delta J^\mu}.$$  

(A.22)

However, the local spin density approximation for relativistic systems is generally not formulated in the context of the current $J^\mu$. Instead one uses the electron density $n (r)$ (2.9) and the magnetization $m (r)$ (2.10)[210].

Instead of expressing the vector potential $A_s^\mu$ by $V_{\text{xc}}$ and $B_{\text{xc}}[210]$, we have used a modified form of the Dirac equation (2.2)[211], where the term describing the interaction with the external magnetic field is not Lorentz invariant. This is related to the fact that the spin of a relativistic electron can only be defined in its rest frame, since the correct quantum number describing it in a spherically symmetric potential is the total angular momentum $J = L + S$. Regardless of this issue, (2.2) represents a good approximation of (A.19) in weak magnetic fields, which is the common situation in solid state physics. The approximation only neglects terms which are higher order in the vector potential such as the diamagnetic contribution, but it does not affect the spin–orbit coupling, which is essential for the relativistic description of magnetic interactions.

### A.7 The single-particle Green function

In this section we will discuss scattering theory summarized in section 2.2. Consider the stationary single-particle Schrödinger equation such as (2.2),

$$(\varepsilon_n - H) \psi_n = 0,$$  

(A.23)

with $H$ being the Hamiltonian of the system over a Hilbert space $\mathcal{H}$, $\psi_n \in \mathcal{H}$ an eigenvector and $\varepsilon_n$ an eigenvalue of $H$.

The resolvent operator $G (z)$ is defined as

$$(z - H) G (z) = I,$$  

(A.24)

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where \( I \) is the identity operator. The set of \( z \in \mathbb{C} \) values for which \( G(z) \) is a bounded linear operator is called the resolvent set, denoted by \( \varrho \left( H \right) \). Its complementer set \( \sigma \left( H \right) = \mathbb{C}/\varrho \left( H \right) \) is called the spectrum of \( H \), which contains the eigenvalues of \( H \).

The spectrum of \( H \) may also contain elements \( \varepsilon_n \) for which (A.23) does not hold, but there exists a sequence \( \{ \psi_{n,i} \}_{i=1}^{\infty} \subset \mathcal{H} \) such that

\[
\lim_{i \to \infty} \| (\varepsilon_n - H) \psi_{n,i} \| = 0. \tag{A.25}
\]

These elements \( \varepsilon_n \) form the continuous spectrum of \( H \). Since \( H \) is a self-adjoint operator, \( \sigma \left( H \right) \subset \mathbb{R} \). The spectral theorem states that it also has a spectral decomposition of the form

\[
H = \int_{-\infty}^{\infty} \varepsilon \, dE(\varepsilon), \tag{A.26}
\]

where \( dE(\varepsilon) \) is a projector-valued measure. We will replace it by its more common form in physics literature,

\[
H = \sum_{\varepsilon_n \in \sigma \left( H \right)} \varepsilon_n |\psi_n\rangle \langle \psi_n|. \tag{A.27}
\]

If \( \psi_n \) is an eigenvector, \( |\psi_n\rangle \langle \psi_n| \) is an orthogonal projection onto the subspace of \( \psi_n \). However, the sum in (A.27) is meant to also include an integration over the continuous part of the spectrum.

In the spectral representation, the identity and the resolvent operators are given by

\[
I = \sum_{n} |\psi_n\rangle \langle \psi_n|, \tag{A.28}
\]

\[
G(z) = \sum_{n} \frac{1}{z - \varepsilon_n} |\psi_n\rangle \langle \psi_n|. \tag{A.29}
\]

Equation (A.28) is also known as the completeness relation.

The coordinate representation of \( G(z) \) is the Green function of the Schrödinger equation (2.12), given in spectral representation as

\[
G(z; \mathbf{r}, \mathbf{r}') = \sum_{n} \frac{1}{z - \varepsilon_n} \psi_n(\mathbf{r}) \psi_n^\dagger(\mathbf{r}). \tag{A.30}
\]

As mentioned in section 2.2, the Green function is not well-behaved along the real axis, because it is not defined for \( z \in \sigma \left( H \right) \). For values \( \varepsilon \in \mathbb{R} \), the Green function is characterized by the limits of \( G(z; \mathbf{r}, \mathbf{r}') \) from the direction of positive and negative imaginary parts of \( z \),

\[
G^+(\varepsilon; \mathbf{r}, \mathbf{r}') = \lim_{\delta \to 0^+} G(\varepsilon + i\delta; \mathbf{r}, \mathbf{r}') = \lim_{\delta \to 0^+} \sum_{n} \frac{1}{\varepsilon - \varepsilon_n + i\delta} \psi_n(\mathbf{r}) \psi_n^\dagger(\mathbf{r}'), \tag{A.31}
\]

\[
G^-(\varepsilon; \mathbf{r}, \mathbf{r}') = \lim_{\delta \to 0^+} G(\varepsilon - i\delta; \mathbf{r}, \mathbf{r}') = \lim_{\delta \to 0^+} \sum_{n} \frac{1}{\varepsilon - \varepsilon_n - i\delta} \psi_n(\mathbf{r}) \psi_n^\dagger(\mathbf{r}'). \tag{A.32}
\]

The functions (A.31) and (A.32) are called retarded and advanced Green functions, respectively. The imaginary part of the Green function may be expressed as

\[
iG^+(\varepsilon; \mathbf{r}, \mathbf{r}') - iG^-(\varepsilon; \mathbf{r}, \mathbf{r}') = -2\text{Im} G^+(\varepsilon; \mathbf{r}, \mathbf{r}') = \sum_{n} 2\pi\delta(\varepsilon - \varepsilon_n) \psi_n(\mathbf{r}) \psi_n^\dagger(\mathbf{r}'). \tag{A.33}
\]
This quantity is also known as the spectral function, which identifies the particles in the system. Since we consider a noninteracting system, all particles have infinite lifetime, indicated by the Dirac delta distributions with zero width. The expectation value of single-particle operators (2.13) is expressed by the spectral function.

### A.8 Calculation of the Green function by the Körringa–Kohn–Rostoker method

The calculation of the Green function (A.30) requires the knowledge of all eigenvectors and eigenvalues of the Hamiltonian. It is advisable to decompose the Hamiltonian of the system into two parts,

\[ H = H_0 + V, \]

where the reference system \( H_0 \) is exactly solvable, usually representing free electrons. Then the correspondence between the full resolvent \( G (z) \) and the resolvent of the reference system \( G_0 (z) \) is given by the Dyson equation,

\[ G (z) = (I - G_0 (z) V)^{-1} G_0 (z). \]

One can also define the \( T \) operator which sums up all effects of the potential \( V \) as

\[ T (z) = (I - V G_0 (z))^{-1} V. \]

This operator enables the simpler calculation of the Green function by using the equation

\[ G (z) = G_0 (z) + G_0 (z) T (z) G_0 (z), \]

meaning that all single-particle expectation values as in (2.13) may also be expressed using the coordinate representation of the \( T \) operator.

As discussed in section 2.2, the potential \( V \) is decomposed into atomic cells within the Körringa–Kohn–Rostoker method. The \( T \) operator may be decomposed similarly. The single-site \( t \) operator

\[ t_i = (I - V_i G_0)^{-1} V_i \]

contains the effects of scattering events on the same site, while the scattering path operator \( \tau \)

\[ \tau_{ij} = t_i \delta_{ij} + \sum_k t_i G_0 (1 - \delta_{ik}) \tau_{kj}, \]

includes the scattering effects between the sites. Since \( \tau \) determines the full \( T \) operator through

\[ T = \sum_{ij} \tau_{ij}, \]

the operators \( t \) and \( \tau \) provide a complete description of the system. The equivalent of the Dyson equation (A.37) for the solutions of the Kohn–Sham–Dirac equation is the Lippmann–Schwinger equation

\[ \psi_i^\pm (\varepsilon) = \psi_{0,i} (\varepsilon) + G_0^\pm (\varepsilon) t_i^\pm (\varepsilon) \psi_{0,i} (\varepsilon), \]
where the real-axis limits of the $t$ operators $t^+_i$ are defined analogously to the retarded and advanced Green functions in (A.31)-(A.32). For the spherically symmetric case, the solutions $\psi^\pm_i(\varepsilon)$ will be denoted by $R^Q_i$, where $Q$ is the quantum number of the total angular momentum operator $J$. Outside the atomic sphere $i$, the Lippmann–Schwinger equation in coordinate representation takes the form

$$R^Q_i(\varepsilon; \mathbf{r}_i) = J^Q(\varepsilon; \mathbf{r}_i) - i\hbar \sum_{Q'} H^{+Q'}(\varepsilon; \mathbf{r}_i) t^{Q'Q}_i(\varepsilon).$$  \hspace{1cm} (A.42)

Here $\mathbf{r}_i$ denotes the position vector with respect to the centre of the atomic sphere, $t^{Q'Q}_i$ is the matrix representation of the $t$ operator, while $J^Q$ and $H^{+Q'}$ are the solutions of the free Kohn–Sham–Dirac equation, and therefore consist of products of spinors, spherical harmonics and spherical Bessel and Hankel functions[41]. The coefficient $p$ is defined as the solution of

$$\varepsilon^2 = p^2 c^2 + m^2 c^4, \quad \text{Im} p > 0. \hspace{1cm} (A.43)$$

The prescription $\text{Im} p > 0$ is necessary to obtain the correct expression for the Green function as $\varepsilon$ approaches the real axis. It should be noted that while the Kohn–Sham–Dirac equation only has regular solutions for $\varepsilon \in \sigma (H)$ – since it is the eigenvalue equation of the Hamiltonian $H$ –, the $t$ operator and the Green function are only defined on the completer set $\varepsilon \in \varrho (H)$. Therefore, the eigenvalue equation must formally be solved for complex $\varepsilon$ values, which will generally lead to solutions which are unbounded at $r \to \infty$; however, these unbounded solutions are only considered inside the atomic cells.

During the calculations, the solutions $R^Q_i$ are determined numerically and then $t^{Q'Q}_i$ is evaluated on the basis of equation (A.42). In practice this means a matching of the solutions at the surface of the atomic sphere to the free solutions outside the cell. For example, in the nonrelativistic case the quantum number $Q$ is replaced by the angular momentum quantum numbers $lm$, and the $t$-matrix is expressed as

$$t^{lm,lm'}_i(\varepsilon) = \frac{1}{\hbar} \delta^{ll'} e^{i\delta^l(\varepsilon)} e^{-i\delta^l(\varepsilon)} \sin \delta^l(\varepsilon), \hspace{1cm} (A.44)$$

where $\delta^l(\varepsilon)$ is the phase shift of nonrelativistic, spherically symmetric potential scattering.

Finally, the connection between the solutions of the Kohn–Sham–Dirac equation $R^Q_i$ (A.42) and the functions $Z^Q_i$ in (2.21) is given by

$$Z^Q_i(\varepsilon; \mathbf{r}) = \sum_{Q'} R^Q_i(\varepsilon; \mathbf{r}) t^{Q'Q}_i(\varepsilon). \hspace{1cm} (A.45)$$

### A.9 Correspondence between the second derivatives from the \textit{ab initio} calculations and the model Hamiltonian

In this section we will describe the numerical procedure of determining the model parameters in the Hamiltonian in section 2.6.

For determining the $J^A_{ij}$ parameters in (2.36), it is advisable to start with the expressions (2.45)-(2.48). These only contain a single pair of atoms, unlike the sums in (2.49)-(2.50). Introduce the tensor product of the vectors $e_{ri}$,

$$\mathbf{v}_{ri,pj} = (-1)^{r+p} e_{ri} \otimes e_{pj}, \hspace{1cm} (A.46)$$

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and denote the calculated second derivatives by

\[ x_{ri,pj} = \frac{\partial^2 H}{\partial \beta_{pj} \partial \beta_{ri}}, \]  

where \( r = 3 - r \) denotes the opposite angle index. Now equations (2.45)-(2.48) read

\[ v_{ri,pj}J_{ij} = x_{ri,pj}, \]  

where \( J_{ij} \) is represented as a vector in the tensor product space and the left-hand side denotes a scalar product. Equation (A.48) can be rewritten as a system of linear equations,

\[ V_{ri,pj}J_{ij} = x_{ri,pj}v_{ri,pj}, \]  

with \( V_{ri,pj} = v_{ri,pj} \circ v_{ri,pj} \) the orthogonal projection onto the subspace of \( v_{ri,pj} \). Since \( V_{ri,pj} \) is a rank 1 matrix, (A.49) does not have a unique solution. However, one can sum up the contributions from the second derivatives as

\[ \sum_{r,p} V_{ri,pj}J_{ij} = \sum_{r,p} x_{ri,pj}v_{ri,pj}. \]  

Here \( \sum_{r,p} V_{ri,pj} \) has rank 4, which is still not sufficient to determine all the elements of \( J_{ij} \) uniquely. For example, if \( S_i \) and \( S_j \) are parallel to the z axis, (A.50) allows the calculation of \( J^{xx}_{ij}, J^{xy}_{ij}, J^{yy}_{ij} \), and \( J^{yy}_{ij} \), but not the other 5 elements[51]. Therefore, the second derivatives have to be determined for several independent spin directions, and (A.50) summed up over these different calculations indexed by \( t \),

\[ \sum_{r,p,t} V^{(t)\,ri,pj}J_{ij} = \sum_{r,p,t} x^{(t)\,ri,pj}v^{(t)\,ri,pj}. \]  

In order to obtain a rank 9 matrix on the left-hand side, which allows the unique determination of \( J_{ij} \) by solving the linear equation (A.51), the calculations have to be performed for at least three linearly independent spin directions.

For the on-site anisotropy, one has to rely on (2.49)-(2.51) by writing

\[ 2(v_{1i,1i} - v_{2i,2i})K_i = w_{1i}K_i = y_{1i} = x_{1i,1i} - x_{2i,2i}, \]  

\[ (v_{1i,2i} + v_{2i,1i})K_i = w_{2i}K_i = y_{2i} = x_{1i,2i}. \]  

Note that \( w_{1i}, w_{2i} \) are symmetric, traceless tensors; therefore, only the symmetric, traceless part of \( K_i \) may be determined, in agreement with the symmetry properties of the on-site anisotropy tensor discussed in section 2.6.

A symmetric, traceless tensor \( K_i \) may be fully described by 5 independent elements, which can be composed into a vector as

\[ \vec{K}_i = (K^{xx}_i, K^{yy}_i, K^{xy}_i, K^{xz}_i, K^{yz}_i). \]  

Introducing

\[ \tilde{w}_{ri} = (w^{xx}_{ri} + w^{yy}_{ri}, 2w^{yy}_{ri}, w^{xx}_{ri}, 2w^{xx}_{ri}, \)  

\[ e^{yz}_{ri}, 2w^{yz}_{ri}, 2w^{xz}_{ri}, 2w^{yz}_{ri}), \]  

equations (A.52)-(A.53) may be rewritten as

\[ w_{ri}K_i = \tilde{w}_{ri}\vec{K}_i = y_{ri}, \]  

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where the scalar products are evaluated the usual way, but while the original vectors have 9 components, the new vectors only have 5. Now, the vector \( \mathbf{K}_i \) may be obtained in the same way as \( \mathbf{J}_{ij} \); the calculations have to be performed for at least 3 independent spin directions, since a rank 5 matrix has to be constructed from two rank 1 matrices per spin direction. Finally, \( \mathbf{K}_i \) may be restructured from \( \mathbf{K}_i \) as a symmetric, traceless matrix.

Note that the above procedure does not determine the coupling coefficients unambiguously, as there are multiple options for choosing the different spin directions. The result will depend on the choice of these directions because the full interacting spin system is not perfectly described by the Hamiltonian (2.36), it may also contain higher order terms. However, the obtained coupling constants and on-site anisotropy tensors must reflect the symmetry of the considered system. For this purpose, one has to fix the spin directions such a way that they are parallel to symmetry axes of the crystal, and perform the calculations for all nonequivalent symmetry directions. For example, in the case of a triangular lattice monolayer, four calculations have to be performed: three for spins pointing towards the nearest neighbours in the plane and one for spins pointing perpendicularly to the plane; these orientations will ensure that the coupling tensors will have the necessary symmetries.
Appendix B

Calculations based on the spin Hamiltonian

B.1 Rotated coordinate system

In this section we will give an explicit form of the spin components and interaction tensors in the local coordinate system where all spins are parallel to the $z$ axis. This forms the basis of the calculation of the spin wave spectrum in section 3.3.

Starting from the spin variables satisfying (3.21), we will introduce the rotated spins as

$$
\tilde{S}_i^α = R_i^{αβ} S_i^β, \\
S_i^α = R_i^{-αβ} \tilde{S}_i^β,
$$

where $R_i^{αβ}$ is an orthogonal transformation. Then the Poisson brackets read

$$
\{\tilde{S}_i^α, \tilde{S}_j^β\} = \{R_i^{αα'} S_i^{α'}, R_j^{ββ'} S_j^{β'}\} = -\frac{\gamma}{M_i} \varepsilon^{αβγ} δ_{ij} S_i^{γ'}.
$$

The determinant of the orthogonal transformation may be calculated as

$$
\frac{1}{6} \varepsilon^{αβγ} \varepsilon^{α'β'γ'} R_i^{αα'} R_i^{ββ'} R_i^{γγ'} = \det R_i,
$$

which can be rearranged in the form

$$
\varepsilon^{αβγ} R_i^{αα'} R_i^{ββ'} = \varepsilon^{αβγ} R_i^{γγ'} \det R_i.
$$

For a proper rotation with $\det R_i = 1$ we have

$$
\{\tilde{S}_i^α, \tilde{S}_j^β\} = -\frac{\gamma}{M_i} \varepsilon^{αβγ} δ_{ij} R_i^{γγ'} S_i^{γ'} = -\frac{\gamma}{M_i} \varepsilon^{αβγ} δ_{ij} \tilde{S}_i^{γ'},
$$

meaning that the Poisson brackets are invariant under the transformation where the coordinate systems are rotated at each lattice point differently.

If the value of the spin at lattice point $i$ in the ground state is $S_i^{(0)} = \left( S_i^x(0), S_i^y(0), S_i^z(0) \right)$ in the global coordinate system, then one way to construct a proper rotation where $\tilde{S}_i^{(0)} = (0, 0, 1)$ in the local coordinate system is

$$
R_i^{αβ} = \begin{bmatrix}
\frac{S_i^z}{s_i^z} & 0 & -\frac{s_i^x}{s_i^z} \\
-\frac{s_i^x}{s_i^z} S_i^z & s_i^x & -\frac{s_i^y}{s_i^z} \\
S_i^x & S_i^y & S_i^z
\end{bmatrix},
$$
where

\[ S_i^{(0)} = \sqrt{1 - (S_i^y)^2}. \]  

(B.8)

Using the model Hamiltonian (3.1), the equation of motion (3.23) reads

\[ \partial_t S_i^\alpha = \frac{7}{M_i} \epsilon^{\alpha \beta \gamma} S_i^\beta J_{ij}^\gamma S_j^\delta + \frac{7}{M_i} \epsilon^{\alpha \beta \gamma} S_i^\beta 2K_{ij}^\delta S_i^\delta - \gamma \epsilon^{\alpha \beta \gamma} S_i^\beta B_i^\gamma, \]  

(B.9)

while in the rotated coordinate system the equation has the same form,

\[ \partial_t \tilde{S}_i^\alpha = \frac{7}{M_i} \epsilon^{\alpha \beta \gamma} \tilde{S}_i^\beta \tilde{J}_{ij}^\gamma \tilde{S}_j^\delta + \frac{7}{M_i} \epsilon^{\alpha \beta \gamma} \tilde{S}_i^\beta 2\tilde{K}_{ij}^\delta \tilde{S}_i^\delta - \gamma \epsilon^{\alpha \beta \gamma} \tilde{S}_i^\beta \tilde{B}_i^\gamma, \]  

(B.10)

with the rotated coefficients

\[ \tilde{J}_{ij}^\gamma = R_i^{\gamma'} R_j^{\delta'} J_{ij}^{\gamma' \delta'}, \]  

(B.11)

\[ \tilde{K}_{ij}^\gamma = R_i^{\gamma'} R_j^{\delta'} K_{ij}^{\gamma' \delta'}, \]  

(B.12)

\[ \tilde{B}_i^\gamma = R_i^{\gamma'} B_i^\gamma. \]  

(B.13)

Note that on a translationally invariant lattice symmetry dictates \( J_{ij}^{\alpha \beta} = J^{\alpha \beta} (R_i - R_j) \). In an incommensurate ground state, this will no longer hold for \( J_{ij}^{\alpha \beta} \), as the magnetic periodicity will differ from the atomic one. However, \( \tilde{J}_{ij}^{\alpha \beta} = \tilde{J}_{ji}^{\beta \alpha} \) still holds, since it is a necessary condition for the existence of the Hamiltonian.

### B.2 Diagonalization of the equation of motion

In this section we will discuss the diagonalization procedure necessary for the calculation of the spin wave frequencies in section 3.3. After Fourier transformation in time \((\partial_t \rightarrow -i\omega)\), (3.36) transforms into the eigenvalue equation

\[ \omega \begin{bmatrix} q \\ p \end{bmatrix} = - \begin{bmatrix} 0 & -1 \\ i & 0 \end{bmatrix} \begin{bmatrix} C & B^T \\ B & A \end{bmatrix} \begin{bmatrix} q \\ p \end{bmatrix} = -\sigma_y H_{SW} \begin{bmatrix} q \\ p \end{bmatrix}, \]  

(B.14)

with \( \sigma_y \) the Pauli matrix expanded to the \( 2N \times 2N \)-dimensional space and \( H_{SW} \) the matrix appearing on the right-hand side of (3.31).

Since the ground state is a stable equilibrium state, \( H_{SW} \geq 0 \) holds, and therefore \( H_{SW}^{1/2} \) exists and is an invertible matrix. Then \( -\sigma_y H_{SW} \) is connected to \( -H_{SW}^{1/2} \sigma_y H_{SW}^{1/2} \) via a similarity transformation, meaning that the two matrices have the same eigenvalues.

Since \( -H_{SW}^{1/2} \sigma_y H_{SW}^{1/2} \) is a self-adjoint matrix, it only has real eigenvalues, which we can denote by \( \omega_k, k = 1, \ldots, 2N \). If \( \omega_k \) is an eigenvalue of \( -\sigma_y H_{SW} \), then from (3.36) \(-i\omega_k \) is an eigenvalue of a real-valued matrix, which means that the eigenvalues always appear in \( \pm \omega_k \) pairs. If \( H_{SW} \) is not strictly positive definite but has zero eigenvalues, then \( -\sigma_y H_{SW} \) has the same number of zero eigenvalues, and one can perform the above similarity transformation on the subspace which does not contain the eigenvectors with zero eigenvalues.

In the next step we consider the eigenvectors of the matrix \( -\sigma_y H_{SW} \). In specific cases, finding the eigenvectors constitutes of Fourier transformation as for the ferromagnetic system in section 3.1. The condition for this is that not only the lattice, but also...
the ground state must exhibit discrete translational symmetry, otherwise Fourier transformation does not diagonalize the $A, B, C$ matrices. Generally, Fourier transformation cannot be applied for incommensurate spin structures.

Since $-\sigma_y H_{SW}$ can be diagonalized as discussed above, it has the form

$$-\sigma_y H_{SW} = V^{-1}DV,$$  \hspace{1cm} (B.15)

where $D = \text{diag}(\omega_k, k = 1, \ldots, 2N)$. Equation (B.15) can be reformulated as

$$\begin{align*}
\omega_k V_{q,k}^{-1} &= iB_{ij} V_{q,k}^{-1} + iA_{ij} V_{p,jk}^{-1}, \\
\omega_k V_{p,k}^{-1} &= -iC_{ij} V_{q,k}^{-1} - iB_{ji} V_{p,jk}^{-1}, \\
\omega_k V_{kj} &= iV_{q,k} B_{ij} - iV_{kp} C_{ij}, \\
\omega_k V_{kp} &= iV_{q,k} A_{ij} - iV_{kp} B_{ji}.
\end{align*}$$  \hspace{1cm} (B.16)-(B.19)

The eigenvectors have to satisfy

$$V_{q,k} V_{q,k'}^{-1} + V_{p,k} V_{p,k'}^{-1} = \delta_{kk'},$$  \hspace{1cm} (B.20)

since $VV^{-1} = I$. It is easy to prove that (B.20) always gives zero if $\omega_k \neq \omega_{k'}$, by the standard argument of multiplying (B.16) and (B.17) by $V_{k,q}$ and $V_{k,p}$, and performing the summation. For $\omega_k = \omega_{k'}$ it is possible to decompose a degenerate subspace to obtain $\delta_{kk'}$, as (B.20) cannot give 0 for all $k'$ values for a fixed $k$, since that would mean that one of the eigenvectors is 0.

Now we will show that (B.20) can be satisfied with a further constraint on the matrices $V$ and $V^{-1}$,

$$V_{q,k} = -i\alpha_k V_{p,k}^{-1}, \quad V_{p,k} = i\alpha_k V_{q,k}^{-1},$$  \hspace{1cm} (B.21)

where $\alpha_k$ may be 1 or $-1$. Substituting (B.21) into (B.18)-(B.19) and taking the conjugate shows that this is an eigenvector from the right if and only if $V_{(q,p)k}^{-1}$ is an eigenvector from the left. From (B.20) we know that there exists a matrix $V'_{k(q,p)}$ such that

$$V'_{q,k} V_{q,k}^{-1} + V'_{p,k} V_{p,k}^{-1} = 1.$$  \hspace{1cm} (B.22)

Since the nondegenerate eigenvectors are fixed apart from multiplication by a nonzero constant, by $V'_{k(q,p)k} = cV_{k(q,p)k}$ we have

$$c \left( V_{q,k} V_{q,k}^{-1} + V_{p,k} V_{p,k}^{-1} \right) = 1 = c\alpha_k \left( -iV_{p,k}^{-1} V_{q,k}^{-1} + iV_{q,k}^{-1} V_{p,k}^{-1} \right).$$  \hspace{1cm} (B.23)

Since the ellipses on the right-hand side contain a real number, $c$ will also be real. We can set $c = 1$ by rescaling $V_{k(q,p)k}$ and $V_{(q,p)k}^{-1}$ by $1/\sqrt{|c|}$, and including the sign in $\alpha_k$.

The value of $\alpha_k$ can be calculated as follows. Since $H_{SW} \geq 0$, we have by (B.16)-(B.19) and (B.21)

$$V_k^{-1} H_{SW} V_k^{-1} = \alpha_k \omega_k \left( V_{q,k} V_{q,k}^{-1} + V_{p,k} V_{p,k}^{-1} \right) \geq 0.$$  \hspace{1cm} (B.24)

Since we set $(V_{q,k} V_{q,k}^{-1} + V_{p,k} V_{p,k}^{-1}) = 1$, we get $\alpha_k = 1$ if $\omega_k > 0$ and $\alpha_k = -1$ otherwise.

From now on, $V_{(q,p)k}$ will denote an eigenvector with eigenvalue $\omega_k \geq 0$ and $V_{(q,p)k}^{-1}$ for the same $k = 1, \ldots, N$ an eigenvector with eigenvalue $-\omega_k \leq 0$. By the above argument we have

$$V_{q,k} = -iV_{p,k}^{-1}, \quad V_{p,k} = iV_{q,k}^{-1};$$  \hspace{1cm} (B.25)

$$V_{k,q} = iV_{p,k}^{-1}, \quad V_{k,p} = -iV_{q,k}^{-1}. $$  \hspace{1cm} (B.26)
By taking the conjugates of (B.16)-(B.17), it is straightforward to see that we can also set

$$V_{q,k\downarrow}^{-1} = V_{q,k\uparrow}^{-1*}, \quad V_{p,k\uparrow}^{-1} = V_{p,k\downarrow}^{-1*}. \tag{B.27}$$

Next we introduce the new observables

$$a_{k\uparrow} = V_{k\uparrow q_i} q_i + V_{k\uparrow p_i} p_i. \tag{B.28}$$

By conjugation we have

$$a_{k\uparrow}^* = V_{k\uparrow q_i}^* q_i + V_{k\uparrow p_i}^* p_i = V_{k\downarrow q_i} q_i + V_{k\downarrow p_i} p_i = a_{k\downarrow}, \tag{B.29}$$

so the inverse transformation can be written as

$$q_i = V_{q,k\uparrow}^{-1} a_{k\uparrow} + V_{q,k\downarrow}^{-1} a_{k\downarrow} = V_{q,k\uparrow}^{-1} a_{k\uparrow} + V_{q,k\uparrow}^{-1*} a_{k\uparrow}^*, \tag{B.30}$$

$$p_i = V_{p,k\uparrow}^{-1} a_{k\uparrow} + V_{p,k\downarrow}^{-1} a_{k\downarrow} = V_{p,k\uparrow}^{-1} a_{k\uparrow} + V_{p,k\uparrow}^{-1*} a_{k\uparrow}^*, \tag{B.31}$$

which will always lead to real-valued quantities $q_i$ and $p_i$. By using (B.25)-(B.27) and the canonical Poisson brackets (3.28), it is easy to see that

$$\{a_{k\uparrow}, a_{k'\uparrow}\} = -i\delta_{kk'}, \tag{B.32}$$

$$\{a_{k\uparrow}, a_{k'\downarrow}\} = 0, \tag{B.33}$$

meaning that $a_{k\uparrow}$ is the classical equivalent of a bosonic operator, and

$$\{q_i, p_j\} = \delta_{ij} = V_{q,k\uparrow}^{-1} V_{k\uparrow q_j} + V_{q,k\downarrow}^{-1} V_{k\downarrow q_j} = V_{p,k\uparrow}^{-1} V_{k\uparrow p_j} + V_{p,k\downarrow}^{-1} V_{k\downarrow p_j}, \tag{B.34}$$

$$\{q_i, q_j\} = 0 = -V_{q,k\uparrow}^{-1} V_{k\uparrow q_j} - V_{q,k\downarrow}^{-1} V_{k\downarrow q_j} = V_{p,k\uparrow}^{-1} V_{k\uparrow p_j} + V_{p,k\downarrow}^{-1} V_{k\downarrow p_j}, \tag{B.35}$$

that is, $V^{-1} V = I$ as it should be.

By substituting (B.28)-(B.29) into (3.36), one can see that the new observables satisfy the trivial equations of motion (3.38)-(3.39). By substituting the inverse transformation (B.30)-(B.31) into (3.31) and using (B.25)-(B.27), it can be proven directly that the Hamiltonian transforms into (3.40) and no additive constant appears in the expression.

The transformation matrices $V$ and $V^{-1}$ also play an important role in calculating perturbative corrections to the free energy as discussed in section 4.1. Using (B.30)-(B.31), the expectation value of the products of the coordinates and the momenta is given by

$$\langle q_i q_j \rangle_{SW} = \sum_k \left( V_{q_i,k\uparrow}^{-1} V_{q_j,k\uparrow}^{-1*} + V_{q_i,k\downarrow}^{-1} V_{q_j,k\downarrow}^{-1*} \right) n_k, \tag{B.36}$$

$$\langle q_i p_j \rangle_{SW} = \sum_k \left( V_{q_i,k\uparrow}^{-1} V_{p_j,k\uparrow}^{-1*} + V_{q_i,k\downarrow}^{-1} V_{p_j,k\downarrow}^{-1*} \right) n_k, \tag{B.37}$$

$$\langle p_i p_j \rangle_{SW} = \sum_k \left( V_{p_i,k\uparrow}^{-1} V_{p_j,k\uparrow}^{-1*} + V_{p_i,k\downarrow}^{-1} V_{p_j,k\downarrow}^{-1*} \right) n_k, \tag{B.38}$$

where $n_k$ is the spin wave occupation number in (4.3) and (4.5). Since the higher-order corrections $H_1$ to the Hamiltonian in section 4.1 are usually expressed in the $q_i, p_i$ variables, while the Hamiltonian is diagonal in the variables $a_{k\uparrow}$, one has to rely on (B.36)-(B.38) when numerically determining the perturbation matrix $P_{kk'}$ in (4.9).
B.3 Derivation of the mean-field Curie temperature for spin reorientation transitions

In the ferromagnetic model in section 4.3, it is sufficient to consider mean-field spin configurations where the magnetization points in the same direction at every lattice point, $\langle S_1^\alpha \rangle = \langle S^\alpha \rangle$, covering all possible ferromagnetic states and the paramagnetic one. The stability of the paramagnetic solution can be determined by expanding the free energy (4.18) around $\langle S^\alpha \rangle = 0$ up to second-order terms in the magnetizations,

$$
\frac{2}{N} F_{\text{MF}} \approx - z (J + \Delta J) \langle S^z \rangle^2 \left( \frac{1}{k_B T} \right)^2 \int (S_i^z)^2 e^{-\frac{1}{k_B T} K^{zz}(S_i^z)^2} dS_i \left( \frac{1}{k_B T} \right)^2 \int (S_i^z)^2 e^{-\frac{1}{k_B T} K^{zz}(S_i^z)^2} dS_i
$$

$$
\times \left( \int e^{-\frac{1}{k_B T} K^{zz}(S_i^z)^2} dS_i \right)^{-1} - z J \langle S^z \rangle \left( \frac{1}{k_B T} \right)^2 \int (S_i^z)^2 e^{-\frac{1}{k_B T} K^{zz}(S_i^z)^2} dS_i \left( \frac{1}{k_B T} \right)^2 \int (S_i^z)^2 e^{-\frac{1}{k_B T} K^{zz}(S_i^z)^2} dS_i)^{-1} - z J \langle S^y \rangle^2
$$

$$
- \frac{1}{k_B T} z^2 J^2 \langle S^y \rangle^2 \int (S_i^y)^2 e^{-\frac{1}{k_B T} K^{zz}(S_i^y)^2} dS_i \left( \frac{1}{k_B T} \right)^2 \int (S_i^y)^2 e^{-\frac{1}{k_B T} K^{zz}(S_i^y)^2} dS_i)^{-1}. \quad (B.39)
$$

For $K^{zz} = 0$, the paramagnetic state is stable against perturbations of the form $\langle S^z \rangle \neq 0$ for temperatures

$$
k_B T > -\frac{1}{3} z (J + \Delta J), \quad (B.40)
$$

and against $\langle S^x \rangle \neq 0$ for

$$
k_B T > -\frac{1}{3} z J. \quad (B.41)
$$

Note that for $J < 0$ and $\Delta J > 0$, (B.41) is the stronger criterion, which simply determines the well-known mean-field Curie temperature of the classical Heisenberg model – see e.g. [57].

For a finite value of $K^{zz}$, it is advisable to expand the integrals in (B.39) in the small parameter

$$
\frac{K^{zz}}{k_B T} \approx \frac{K^{zz}}{k_B T_c} = \frac{3K^{zz}}{z |J|}. \quad (B.42)
$$

This leads to

$$
\int (S_i^z)^2 e^{-\frac{1}{k_B T} K^{zz}(S_i^z)^2} dS_i \left( \frac{1}{k_B T} \right)^2 \int (S_i^z)^2 e^{-\frac{1}{k_B T} K^{zz}(S_i^z)^2} dS_i)^{-1} \approx \frac{1}{3} + \frac{4}{15} \frac{K^{zz}}{z J}, \quad (B.43)
$$

$$
\int (S_i^x)^2 e^{-\frac{1}{k_B T} K^{zz}(S_i^x)^2} dS_i \left( \frac{1}{k_B T} \right)^2 \int (S_i^x)^2 e^{-\frac{1}{k_B T} K^{zz}(S_i^x)^2} dS_i)^{-1} \approx \frac{1}{3} - \frac{2}{15} \frac{K^{zz}}{z J}. \quad (B.44)
$$

Substituting (B.43)-(B.44) into (B.39) yields the stability criteria (4.21)-(4.22) after minimization with respect to the parameters.
B.4 Spin wave spectra of the ferromagnetic and spin spiral states

Here we will derive the spin wave spectra (6.5) and (6.10) in section 6.2. For the ferromagnetic state, (3.36) takes the form

\[
\begin{align*}
\frac{M}{\gamma} \partial_t q_i &= \sum_j J_{ij} (p_j - p_i) - \sum_j D_{ij} q_j - 2K^{xx} p_i, \\
\frac{M}{\gamma} \partial_t p_i &= -\sum_j J_{ij} (q_j - q_i) - \sum_j D_{ij} p_j + 2K^{xx} q_i.
\end{align*}
\] (B.45) (B.46)

The magnitude of the spins \(M\) is the same for all atoms, since they are in equivalent positions. The equations of motion (B.45)-(B.46) can be decoupled in lattice indices using Fourier transformation,

\[
\begin{align*}
q_k &= \frac{1}{\sqrt{N}} \sum_i e^{-ikR_i} q_i, \\
p_k &= \frac{1}{\sqrt{N}} \sum_i e^{-ikR_i} p_i.
\end{align*}
\] (B.47) (B.48)

The \(a_{k\dagger}\) variables (3.37) are constructed by the transformation

\[
\begin{align*}
a_{k\dagger} &= q_k + ip_k, \\
a^*_k &= q_k - ip_k.
\end{align*}
\] (B.49) (B.50)

Performing Fourier transformation in time leads to the equation of motion

\[
\omega a_{k\dagger} = \omega_k a_{k\dagger},
\] (B.51)

with the spin wave spectrum (6.5).

For the spin spiral state, (3.36) takes the form

\[
\begin{align*}
\frac{M}{\gamma} \partial_t q_i &= \sum_j J_{ij} (p_j - \cos [k_0 (R_j - R_i)] p_i) \\
&\quad + \sum_j D_{ij} \sin [k_0 (R_j - R_i)] p_i + 2K^{xx} p_i, \\
\frac{M}{\gamma} \partial_t p_i &= \sum_j J_{ij} \cos [k_0 (R_j - R_i)] (q_i - q_j) \\
&\quad - \sum_j D_{ij} \sin [k_0 (R_j - R_i)] (q_i - q_j),
\end{align*}
\] (B.52) (B.53)

The spin spiral state is not invariant under translation by lattice vectors like the ferromagnetic state, it only transforms into itself when displaced by the wavelength of the spiral. However, due to the specific form of (6.1), the Fourier transformation (B.47)-(B.48) will still diagonalize equations (B.52)-(B.53) in site index. Introducing the new variables

\[
\beta_{k\pm} = q_k \pm ip_k,
\] (B.54)

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and performing Fourier transformation in time leads to

\[
C_1 (\mathbf{k}; k_0) = \frac{1}{2} \left\{ J_k + \frac{1}{2} \left[ J_{k+k_0} + J_{k-k_0} \right] - \frac{i}{2} \left[ iD_{k-k_0} - iD_{k+k_0} \right] \right\} - J_k - \text{i}D_{k_0} + K^{xx},
\]

\[
C_2 (\mathbf{k}; k_0) = \frac{1}{2} \left\{ -J_k + \frac{1}{2} \left[ J_{k+k_0} + J_{k-k_0} \right] - \frac{i}{2} \left[ iD_{k-k_0} - iD_{k+k_0} \right] \right\} - K^{xx},
\]

\[
\frac{M}{\gamma} \omega \beta_{k+} = C_1 (\mathbf{k}; k_0) \beta_{k+} + C_2 (\mathbf{k}; k_0) \beta_{k-},
\]

\[
\frac{M}{\gamma} \omega \beta_{k-} = -C_2 (\mathbf{k}; k_0) \beta_{k+} - C_1 (\mathbf{k}; k_0) \beta_{k-}.
\]

The normal frequencies of the system (6.10) are obtained after a further diagonalization step; the connection between (B.55)-(B.56) and (6.8)-(6.9) reads

\[
C_\pm (\mathbf{k}; k_0) = C_1 (\mathbf{k}; k_0) \pm C_2 (\mathbf{k}; k_0).
\]

**B.5 Numerical procedures for anharmonic spin spirals**

In the lattice equivalent of the continuum model in section 6.3, we will consider scalar Heisenberg exchange interactions \( J_{ij} \) as in section 6.2, but replace the \( K^{xx} \) anisotropy by \( K^{zz} < 0 \). Contrary to sections 6.1-6.3, we will suppose that the wave vector of the spiral is along the \( x \) direction, with the spins rotating in the \( xz \) plane. This is only necessary to keep the notations consistent between this section and chapter 10 where the results are applied; there is no fundamental difference between the in-plane \( x \) and \( y \) directions. In this case, the Dzyaloshinsky–Moriya interaction may be characterized by the \( D_{ij}^y = D_{ij} \) component, since this will influence the energy of the cycloidal spiral. As a first step, one has to determine the equilibrium spin spiral configuration; this is performed by writing the equations of motion in the global coordinate system,

\[
\frac{M}{\gamma} \partial_t S_i^x = -\sum_j J_{ij} (S_i^x S_j^y - S_i^y S_j^x) + \sum_j D_{ij} S_i^y S_j^x + 2K^{zz} S_i^z S_j^y,
\]

\[
\frac{M}{\gamma} \partial_t S_i^y = -\sum_j J_{ij} (S_i^y S_j^z - S_i^z S_j^y) - \sum_j D_{ij} (S_i^y S_j^x + S_i^x S_j^y) - 2K^{zz} S_i^x S_j^y,
\]

\[
\frac{M}{\gamma} \partial_t S_i^z = -\sum_j J_{ij} (S_i^y S_j^x - S_i^x S_j^y) + \sum_j D_{ij} S_i^y S_j^x.
\]

A spin spiral state in the \( xz \) plane automatically satisfies (B.60) and (B.62) due to \( S_i^y = 0 \), so the equilibrium condition simplifies to

\[
\frac{M}{\gamma} \partial_t S_i^y = -\sum_j J_{ij} (S_i^y S_j^z - S_i^z S_j^y) - \sum_j D_{ij} (S_i^z S_j^x + S_i^x S_j^z) - 2K^{zz} S_i^x S_j^y = 0. \tag{B.63}
\]

Since the spins are confined to one plane, they can be characterized by a single angle variable \( \vartheta_i \),

\[
S_i = (-\sin \vartheta_i, 0, \cos \vartheta_i).
\]

\[
S_i = (-\sin \vartheta_i, 0, \cos \vartheta_i).
\]

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Furthermore, it is sufficient to solve equation (B.63) for a chain of spins $i = 1, \ldots, L_x$ instead of the full two-dimensional lattice, since the spins are parallel in the direction perpendicular to the wave vector $k_0$. The sign convention of (B.64) corresponds to a left-rotating spin spiral if $\theta_i$ is a monotonically increasing function of $i$; such a rotational sense is preferred by the Dzyaloshinsky–Moriya interaction if we suppose $D_{ij} > 0$ for $R_j^y - R_i^y > 0$.

Substituting (B.64) into (B.63) leads to the equilibrium condition

$$- \sum_j J_{ij} \sin (\theta_j - \theta_i) - \sum_j D_{ij} \cos (\theta_j - \theta_i) + 2K^{zz} \cos \theta_i \sin \theta_i = 0. \quad (B.65)$$

Equation (B.65) must be solved by a numerical procedure. Fortunately, the Landau–Lifshitz–Gilbert equation (5.4) provides a possible algorithm for the solution, since it always converges to stable equilibrium states—see (5.5). Introducing the torque acting on the spins as

$$T_i = S_i \times B_i^{\text{eff}}, \quad (B.66)$$

the Landau–Lifshitz–Gilbert equation simplifies to

$$\partial_t S_i = -\gamma' T_i - \alpha \gamma' S_i \times T_i. \quad (B.67)$$

In (B.67), the relaxation term proportional to $\alpha$ is responsible for the convergence to the energy minimum, and the precession term can be dropped from the equation. In this case, if we consider an initial state where all the spins are in the $xz$ plane, the torque will only have a $y$ component initially, $T_i = (0, T_i^y, 0)$, and it will remain parallel to this direction during the time evolution described by the relaxation term. Therefore, (B.67) will simplify to the equation of motion of the $\theta_i$ variables,

$$\partial_t \theta_i = \alpha \gamma' T_i^y, \quad (B.68)$$

where $T_i^y$ is the left-hand side of (B.65). Due to the reduced number of variables, solving (B.68) is simpler than finding the equilibrium states from spin dynamics simulations performed on a two-dimensional lattice.

After the equilibrium state has been constructed, the energy of the system may be calculated by substituting into (3.1), and the ground state determined by finding the state with the lowest energy. However, this method is only feasible when one has to choose between the ferromagnetic state and several spin spiral states with different wavelengths. If neither the wave vector direction nor the rotational plane of the spiral is known in advance, it is advisable to use some approximative methods. One such method is calculating the Fourier transform of the exchange interaction tensors,

$$J_i^{\alpha\beta} = \sum_{i-j} J_{ij}^{\alpha\beta} e^{-ik(R_i - R_j)}, \quad (B.69)$$

and determining its eigenvalues and eigenvectors in Cartesian indices[212]. The ideal spin spiral state with the given wave vector may be identified by the lowest eigenvalue, while the eigenvector helps in identifying the plane of the spiral and its rotational sense.

The above discussed method can reproduce the spin spiral energies exactly for some special forms of the Hamiltonian, such as the example (6.6) in section 6.2. Although it is possible to include the on-site anisotropy in (B.69) by setting $J_{ii}^{\alpha\beta} = 2K_{ii}^{\alpha\beta}$, anisotropy
terms are not treated exactly within the method. Generally, the Fourier transform of the exchange interaction matrices produces a lower energy than an actual spin spiral state, since the eigenvectors may contain imaginary components, which do not always correspond to a physical state of the Hamiltonian (3.1) with normalized spin vectors $\mathbf{S}_i$. This problem is escalated when one is dealing with multiple magnetic layers, since the complex eigenvectors in the multi-dimensional space hardly resemble real-space spin configurations.

A possible alternative is calculating the energy of harmonic spin spiral configurations such as (6.1) by substituting into (3.1). Although this solves the problem with nonphysical eigenstates, it will lead to a higher energy than in the ideal case, as the considered configuration is not an equilibrium state of the system. An obvious example is that the on-site energy per spin is $K^{zz}/2$ for any finite wave vector $\mathbf{k}_0$, while it discontinuously jumps to $K^{zz}$ in the ferromagnetic state along the easy axis - for relaxed spin spirals, the energy will be a continuous function of the wavelength. Nevertheless, we used these simplifying methods in chapters 9-11 to approximate the energies of spin spiral states.

On the other hand, the spin wave spectrum can only be calculated around the stable equilibrium spin spiral state. Substituting the current notations into (3.36) yields

$$\frac{M}{\gamma} \partial_t q_i = \sum_j J_{ij} (p_j - \cos (\vartheta_j - \vartheta_i) p_i) + \sum_j D_{ij} \sin (\vartheta_j - \vartheta_i) p_i$$

$$- 2K^{zz} \cos^2 \vartheta_i p_i,$$

(B.70)

$$\frac{M}{\gamma} \partial_t p_i = \sum_j J_{ij} (q_i q_j - \cos (\vartheta_j - \vartheta_i) (q_i - q_j)) - \sum_j D_{ij} \sin (\vartheta_j - \vartheta_i) (q_i - q_j)$$

$$+ 2K^{zz} \cos (2\vartheta_i) q_i.$$  

(B.71)

In the case $K^{zz} = 0$, the angle variables correspond to a harmonic spiral $\vartheta_i = k_i R_i$, equations (B.70)-(B.71) may be diagonalized by Fourier transformation, and one obtains the spin wave spectrum (6.8)-(6.10) for $K^{zz} = 0$. For a finite anisotropy value, the spin wave frequencies must be found numerically; however, it is sufficient to deal with a $2L_x \times 2L_x$ matrix, since Fourier transformation may still be performed in the direction perpendicular to the spin spiral wave vector.

Finally, we will shortly discuss how the perturbation theory derived in section 4.1 can be applied to spin spirals. With the notations used in this section, the quartic terms in the Hamiltonian appearing in (4.8) have the form

$$H_1 = \frac{1}{2} \sum_{i,j} (J_{ij} \cos (\vartheta_i - \vartheta_j) + D_{ij} \sin (\vartheta_i - \vartheta_j)) \left[ \frac{1}{4} (q_i^2 q_j^2 + q_i^2 p_j^2 + p_i^2 q_j^2 + p_i^2 p_j^2) \right]$$

$$- \frac{1}{8} (q_i^3 q_j^3 + q_i p_i^2 q_j + q_i q_i q_j p_j^3 + q_i q_j p_i^2 q_j) \right] - J_{ij} \frac{1}{8} (p_i^3 p_j + p_i q_i^2 p_j + p_i p_j^3 + p_i^2 p_j q_i^2)$$

$$+ \sum_i K^{zz} \left[ \cos^2 \vartheta_i \frac{1}{4} (q_i^2 + p_i^2)^2 - \sin^2 \vartheta_i \frac{1}{4} (q_i^4 + q_i^2 p_i^2) \right].$$  

(B.72)

To obtain an expression for the matrix $P_{kk'}$ in (4.9), we have to calculate the expectation value of (B.72) with respect to the spin wave Hamiltonian. Unfortunately, the analytical expressions are hopelessly complicated even for harmonic spin spirals; we only
present them here for the ferromagnetic state along the easy axis with $\vartheta_i \equiv 0$,

$$
\langle H_1 \rangle_{SW} = \frac{1}{2N} \sum_{k,k'} (J_0 + J_{k-k'} - J_k - J_{k'} + 4K^{zz}) n_k n_{k'}.
$$

(B.73)

The Dzyaloshinsky–Moriya term does not appear in (B.73), since it only influences the ferromagnetic state if it is parallel to the magnetization direction as in section 6.2, while it is perpendicular to the z direction in the current model.

## B.6 The effect of the boundary conditions on spin spirals and skyrmion lattices

In chapters 9-11, the simulations were performed on a finite lattice with periodic boundary conditions, which discretizes the values of observable wave vectors $k_0$ in the system. The transition between different wave vectors may only happen by crossing high energy barriers, which leads to hysteresis in the simulations as discussed in sections 10.4 and 11.2.

The metastability of the different states may be understood by analyzing the spin wave spectrum of spirals (6.8)-(6.10) in section 6.2. If the magnitude of the on-site anisotropy $K^{xx}$ is sufficiently low, then the stability condition $C_\perp (k = 0; k_0) \geq 0$ holds not only for the value of $k_0$ minimizing the energy (6.6), but for a whole regime of wave vector values in reciprocal space. All of these spin spiral states with different wave vectors will possess a Goldstone mode, but this mode corresponds to the translation of the spin spiral, which transformation does not change the wave vector. Due to the stability, possible transitions between spin spirals with different wave vectors will correspond to first-order phase transitions. These phase transitions are illustrated in figures 9.11 and 10.10. The stability also explains why spin wave expansion around spin spirals with different wave vectors and the ferromagnetic state $k_0 = 0$ could be applied in section 10.4.

Spin spirals with different wave vectors may also be examined from a topological standpoint. The finite two-dimensional lattice with periodic boundary conditions corresponds to the two-dimensional torus $T^2$. Since all the spins are parallel in the direction perpendicular to the wave vector $k_0$, it is sufficient to deal with a one-dimensional slice of the torus along $k_0$, corresponding to the unit circle $S^1$. Since in the spin spiral state all the spins are confined to a single plane, in this case the spins are mapped to the unit circle $S^1$, while a general state of the classical Heisenberg model is a mapping to the unit sphere $S^2$. When considering all mappings $S^1 \to S^1$, it turns out that the phase of the spin spiral state can only rotate an integer multiple times around the circle. These integers correspond to the wave vectors of the spirals discretized by the finite lattice, the positive and negative values indicating right- and left-rotating spirals, respectively.

Spirals with different wave vectors wind different times around the unit circle; therefore, they cannot be transformed into each other continuously in the continuum description of the system. In the lattice model, such transitions may still occur, since the spins may be rotated arbitrarily at every lattice site. However, rotating the spins at lattice sites in such a way that one adds or removes a wavelength in the spin spiral state requires large angles between the spins at intermediate steps, which indicates an energy cost on the order of the scalar Heisenberg exchange interactions.

Since the spin waves correspond to small-amplitude modulations of the equilibrium state, the stability of the spectrum discussed in section 6.2 dictates that the transition
between different spin spiral states is only possible by large-scale rotations of the spins. During finite-temperature simulations, mainly spin waves with low energy will be generated in the system, and the temperature may be too low to produce a high-energy transition within realistic simulation timescales. Such a strict distinction between spin spirals with different wave vectors does not occur under experimental conditions, since the spiral wavelength may change by winding down the spin configurations at the edges of the finite-sized sample. See figure 9.1 for typical ultrathin film islands in experiments.

The situation with skyrmions is analogous: as it was calculated in section 11.3, creating or destroying a single skyrmion requires crossing an energy barrier proportional to the nearest-neighbour exchange interactions, and such events are rare at low temperature. This explains the unresolved transition regions SS→SkL and FP→SkL in figure 11.4(c): transitions that modify the topological charge of the system are effectively blocked below $T_c$.

In section 11.1 the phase diagram at zero temperature in figure 11.3 was obtained by considering a spin spiral with a fixed wavelength, as well as a skyrmion lattice with a fixed density. The wavelength of the spin spiral ($\lambda = 6.6\text{nm}$) was determined by calculating the Fourier transforms of the exchange matrices as in appendix B.5, and minimizing the energy with respect to the wave vector$^{[26]}$; the energy difference between the ferromagnetic and the spin spiral states was sufficiently large that the imperfect description of the anisotropy terms did not influence the results considerably. Since the (111) surface of the Ir fcc lattice has threefold rotational symmetry, the spin spiral energies are almost isotropic for small wave vectors; this is in contrast with the lower symmetry of the (110) surface of bcc W and Ta. This quasi-isotropy leads to an almost complete degeneracy on a circle in reciprocal space with a fixed radius, which degeneracy can only be lifted by higher-order interactions; however, these were not included in the $ab\ initio$ calculations. Therefore, the direction of the wave vector $k_0$ was also fixed during the calculations, but it is not characteristic of the considered system; the finite size of the simulation cell played a more important role in determining $k_0$ than the actual anisotropy of the coupling tensors in reciprocal space. The lattice constant of the skyrmion lattice was $d_c = 8.7\text{nm}$, corresponding to 32 Ir(111) lattice constants or 16 skyrmions in the $128 \times 128$ lattice. Note that $d_c$ is the distance between the skyrmion cores, which is different from the skyrmion core diameter $d_0$ introduced in section 11.1$^{[172]}$.

Due to the periodic boundary conditions, $\lambda$ and $d_c$ could only change through topological transitions, meaning an addition or removal of a $360^\circ$ domain wall in a spin spiral or a skyrmion. It is known from micromagnetic calculations$^{[99, 105, 213]}$ that both $\lambda$ and $d_c$ depend on the external magnetic field at zero temperature. However, this dependence is strongest close to a critical field value where the spin spiral and skyrmion lattice states become metastable compared to the field-polarized state, and break into $360^\circ$ domain walls and isolated skyrmions, respectively. The spin spiral state was not examined close to this critical field, since it becomes energetically unfavourable compared to the skyrmion lattice at a significantly lower field value$^{[105]}$. For the skyrmion lattice, we performed calculations for different $d_c$ values close to the transition into the field-polarized state. For $B = 3\text{T}$, the lattice with $d_c = 8.7\text{nm}$ had the lowest energy out of the ones commensurate with the $N = 128 \times 128$ lattice; while for $B = 3.2\text{T}$, even the system with a single skyrmion ($d_c = 34.8\text{nm}$) had higher energy than the field-polarized state. This leads us to the conclusion that the divergence of $d_c$ happens in a very short interval of magnetic field, in agreement with$^{[105]}$. This is probably because the divergence of $d_c$ is a consequence of the repulsive interaction between the skyrmions, but this interac-
Figure B.1: Static structure factor $S(k)$ and its variance $\Delta S(k)$ as a function of temperature, displaying the effect of periodic and free boundary conditions. The model system describes the transition from the ferromagnetic to the SS state discussed in section 10.4. The simulations were performed at decreasing the temperature from the paramagnetic phase. At every temperature value, $k_0^2$ represents the wave vector for which $S(k)$ is maximal. The simulation parameters are $J_1 = -2.0$ mRy, $D = 0.4$ mRy, $K_z^2 = -0.22$ mRy and $N = 128 \times 64$. The averaging was performed over a simulation length of $10^6$ steps after a thermalization of $10^5$ steps.

The presence of the free boundaries also induces a gap in the spin wave spectrum, as the direction of the spin at the edges is fixed by the boundary conditions – see (D.21)-(D.23) in appendix D.4. The spiral can no longer propagate freely along the wave vector direction. This effect is illustrated in figure B.1. By calculating $\Delta S(k)$ (7.8) along with $S(k)$ (7.6), one can obtain information about the phase $\vartheta_i$ of the spiral at a given lattice point. If the spiral is moving along the wave vector direction, the phase $\vartheta_i$ is fluctuating,
and the value of the variance $\Delta S (k)$ will be comparable to that of $S (k)$. In systems with real long-range order, the phase parameter is fixed, and $\Delta S (k)$ only takes a macroscopic value close to the transition into the paramagnetic phase, where the fluctuations exert the strongest effect. Therefore, free boundary conditions are advantageous for observing spin spirals in experiments, because the phase of the spiral becomes pinned at the boundaries. This pinning is indicated in figure B.1 by the fact that the fluctuations $\Delta S (k)$ become relatively small below $T \approx 150 \text{K}$. This difference between experiments and Monte Carlo simulations is discussed in detail in [177].

The pinning effectively describes an interaction between the spin spirals and the boundaries. This effect is also observable for skyrmions, see e.g. [215]. If only a few wavelengths of spirals or several skyrmions can fit into the simulated lattice size, the effect of the free boundaries may be comparable in strength to the interactions between skyrmions and spin spirals. Therefore, using periodic boundary conditions is still preferable when describing thermodynamic phases, and we relied on this method during the simulations.
Appendix C

Stochastic methods

C.1 Derivation of the Fokker–Planck equation

When deriving the Fokker–Planck equation (5.11) in section 5.2, we will rely on the mathematical formulation of stochastic differential equations and largely follow [216]. Although Brown[37] originally arrived at the result using elementary methods, the mathematical formulation introduced here can also be applied to the description of rare switching events in appendix C.2, as well as to the numerical solution of the equation in appendices C.3 and C.4. In the following, summation is understood over all lattice point and Cartesian indices appearing in pairs.

Firstly, we will rewrite (5.6) in a form more common in stochastic calculus,

\begin{align*}
\frac{dS_i^\alpha}{dt} = & -\gamma'\varepsilon^{\alpha\beta\gamma} S_i^\beta \left( \mathcal{B}_i^{\text{eff},\gamma} + \alpha \varepsilon^{\gamma\delta\varepsilon} S_i^\delta \mathcal{B}_i^{\text{eff},\varepsilon} \right) dt \\
& - \gamma' \varepsilon^{\alpha\beta\gamma} S_i^\beta \sqrt{2D_i} (\alpha dW_i^\gamma (t) + \alpha \varepsilon^{\gamma\delta\varepsilon} S_i^\delta \circ dW_i^\varepsilon (t)) \\
= & \mathfrak{a}_i^\alpha dt + b_{ij}^{\alpha\beta} \circ dW_j^\beta (t),
\end{align*}

(C.1)

with the coefficients

\begin{align*}
\mathfrak{a}_i^\alpha = & -\gamma'\varepsilon^{\alpha\beta\gamma} S_i^\beta \mathcal{B}_i^{\text{eff},\gamma} - \alpha \gamma' \left( S_i^\beta S_i^\delta \mathcal{B}_i^{\text{eff},\beta} - \mathcal{B}_i^{\text{eff},\alpha} \right), \\
b_{ij}^{\alpha\beta} = & \left[ -\gamma'\varepsilon^{\alpha\beta\gamma} S_i^\gamma \sqrt{2D_i} - \alpha \gamma' \sqrt{2D_i} \left( S_i^\alpha S_i^\beta - \delta^{\alpha\beta} \right) \right] \delta_{ij}.
\end{align*}

(C.2)

(C.3)

The solution of (C.1) corresponds to the solution of the stochastic integral equation

\begin{align*}
S_i^\alpha (t) = S_i^\alpha (t_0) + \int_{t_0}^t \mathfrak{a}_i^\alpha dt' + \int_{t_0}^t b_{ij}^{\alpha\beta} \circ dW_j^\beta (t').
\end{align*}

(C.4)

The main difference compared to deterministic differential equations is the presence of the stochastic integral with respect to the Brownian motion or Wiener process \( W_j^\beta (t) \) on the right-hand side of (C.4). \( W_i^\alpha (t) \) is an almost surely continuous stochastic process starting from \( W_i^\alpha (0) = 0 \), and it has Gaussian distribution with first and second moments

\begin{align*}
\left< W_i^\alpha (t) \right> = & 0, \\
\left< W_i^\alpha (t) W_j^\beta (t') \right> = & \delta_{ij} \delta^{\alpha\beta} \min \{t, t'\}.
\end{align*}

(C.5)

(C.6)
Stochastic integrals in (C.4) may be thought of as a limit of a sum over short time intervals as the length of the intervals goes to zero, analogously to the deterministic Riemann integral. However, due to the properties (C.5)-(C.6), it can be proven that the limit will depend on at which point in the small time interval the integrand $b^{\alpha \beta}_{ij}(t)$ is evaluated. If the lower boundary of the time interval is substituted into $b^{\alpha \beta}_{ij}(t)$, one obtains the Itô integral; on the other hand, evaluating $b^{\alpha \beta}_{ij}(t)$ at the midpoint of the interval yields the Stratonovich interpretation. During the numerical integration of stochastic differential equations, one approximates stochastic integrals with finite sums, and therefore the results obviously depend on the interpretation of the given integral. As discussed in section 5.2, the Stratonovich interpretation corresponds to the correct description of the spin system in the stochastic Landau–Lifshitz–Gilbert equation. However, expectation values are significantly easier to calculate in the Itô form, and these quantities form the basis of most mathematical and physical applications.

Fortunately, (C.1) can be easily transformed into an Itô differential equation,

$$dS_i^\alpha = \left( a_i^\alpha + \frac{1}{2} b^{\beta \gamma}_{kj} \frac{\partial b^{\alpha \gamma}_{ij}}{\partial S_k^\beta} \right) dt + b^{\alpha \beta}_{ij} dW_j^\beta (t), \quad \text{(C.7)}$$

with

$$\frac{1}{2} b^{\beta \gamma}_{kj} \frac{\partial b^{\alpha \gamma}_{ij}}{\partial S_k^\beta} = -2 D_i \gamma^2 (1 + \alpha^2) S_i^\alpha. \quad \text{(C.8)}$$

We emphasize that the Itô equation (C.7) has the same solution as the Stratonovich equation (C.1); it is common in physics literature (see e.g. [84]) to talk about Itô and Stratonovich forms with the same expansion coefficients $a_i^\alpha$ and $b^{\alpha \beta}_{ij}$, which obviously have different solutions.

An Itô differential equation is called a time-homogeneous Itô diffusion if the coefficients $a_i^\alpha$ and $b^{\alpha \beta}_{ij}$ do not depend explicitly on the Brownian motion $W_i^\alpha$ or the time $t$, just on the stochastic process $S_i^\alpha$ [216]. The generator $A$ of the time-homogeneous Itô diffusion (C.7) can be calculated as

$$A = a_i^\alpha \frac{\partial}{\partial S_i^\alpha} + \frac{1}{2} b^{\beta \gamma}_{kj} b^{\alpha \beta}_{ij} \frac{\partial}{\partial S_k^\beta} \frac{\partial}{\partial S_i^\alpha}$$

$$= \left( -\gamma^2 \varepsilon^{\alpha \gamma \beta} S_i^\beta B_i^{\text{eff}, \gamma} - \alpha \gamma^2 \left( S_i^\alpha S_i^\beta B_i^{\text{eff}, \beta} - B_i^{\text{eff}, \alpha} \right) - 2 D_i \gamma^2 (1 + \alpha^2) S_i^\alpha \right) \frac{\partial}{\partial S_i^\alpha}$$

$$+ D_i \gamma^2 (1 + \alpha^2) \left( \delta^{\alpha \beta} - S_i^\alpha S_i^\beta \right) \frac{\partial}{\partial S_i^\alpha} \frac{\partial}{\partial S_i^\beta}, \quad \text{(C.9)}$$

where summation is understood over the lattice index $i$. The generator describes the time evolution of the stochastic process over infinitesimal time intervals, similarly to transition rates in master equations. Using the spherical coordinates (5.12)-(5.14) and substituting in the effective field (3.24), the generator may be rewritten as

$$A = -\frac{\gamma^2}{M_i} \left[ \left( \frac{1}{\sin \theta_i} \frac{\partial H}{\partial \varphi_i} + \alpha \frac{\partial H}{\partial \theta_i} \right) \frac{\partial}{\partial \varphi_i} + \left( -\frac{1}{\sin \theta_i} \frac{\partial H}{\partial \theta_i} + \alpha \frac{1}{\sin^2 \theta_i} \frac{\partial H}{\partial \varphi_i} \right) \frac{\partial}{\partial \varphi_i} \right]$$

$$+ D_i \gamma^2 (1 + \alpha^2) \Delta_i, \quad \text{(C.10)}$$

with $\Delta_i$ the Laplacian in (5.16).
One possible application of the generator of an Itô diffusion is calculating expectation values of stopping times through Dynkin's formula\cite{216}. A stopping time $\tau$ is a nonnegative random variable with the property that at every fixed time $t$, if we know everything about the diffusion up to time $t$ but nothing of the future, we can decide whether $\tau \leq t$ holds or does not hold. For the spin system described by the stochastic Landau–Lifshitz–Gilbert equation, the calculated stopping times generally correspond to switching times between local energy minima of the system – see appendix C.2.

To simplify the notation, in the following we will denote the space of all spin configurations by $\Omega$, its elements by $x = \{ S_i \}$, and the solution of (C.1) at time $t$ by $X_t$. Let $f \in C^2_0 (\Omega)$ a function on the phase space and $\tau$ a stopping time with finite expectation value. Dynkin's formula reads

$$
\mathbb{E}^x (f (X_\tau)) = f (x) + \mathbb{E}^x \left( \int_{t_0}^\tau A f (X_s) \, ds \right),
$$

where $\mathbb{E}^x$ means expectation value calculated when the process starts from the initial spin configuration $x$ at $t = t_0$. How the expectation value of $\tau$ can be determined from (C.11) is discussed in appendix C.2.

Substituting a fixed time $\tau = t$, and differentiating (C.11) with respect to $t$ leads to

$$
\partial_t \mathbb{E}^x (f (X_t)) = \mathbb{E}^x (A f (X_t)).
$$

Kolmogorov's backward equation\cite{216} basically claims that the generator $A$ can be taken outside the expectation value; that is, introducing

$$
\psi (x, t) = \mathbb{E}^x (f (X_t)),
$$

yields the partial differential equation

$$
\partial_t \psi = A \psi, \quad \psi (x, t_0) = f (x).
$$

The physical interpretation of (C.14) is a diffusion equation, since the generator $A$ (C.10) corresponds to the Laplacian. It may also be interpreted as a free Schrödinger equation if $t$ is replaced by $it$. One possible application of Kolmogorov's backward equation is finding the solution of the partial differential equation (C.14) as an expectation value along a stochastic process, (C.13). In this context, the expectation value is generally referred to as a path integral.

Suppose that the stochastic process can be described by a smooth probability density function $P (y, t; x)$ at every time. Then the expectation value (C.13) can be calculated as

$$
\mathbb{E}^x (f (X_t)) = \int f (y) P (y, t; x) \, dy.
$$

Using integration by parts in (C.16), one arrives at the Fokker–Planck equation (5.11), which is also known as Kolmogorov's forward equation.

### C.2 Calculating the switching time for magnetic particles

In chapters 9-11, we have illustrated the problems with metastable states through several examples: the switching time between different local energy minima may be
significantly longer than reasonable timescales available during spin dynamics or Monte Carlo simulations. Here we will calculate the switching time for a simple but exactly solvable case, and obtain the Arrhenius law (12.7) given in section 12.3 in the low-temperature limit.

Such switching processes have been extensively studied in the literature[217, 218] since the derivation of the stochastic Landau–Lifshitz–Gilbert equation (5.6) by Brown[37]. As has been discussed in section 5.2, the equation of motion may be transformed into a Fokker–Planck or Kolmogorov forward equation (5.11), with a stationary solution corresponding to the Boltzmann distribution. The deviations from this distribution decay exponentially, described by the negative eigenvalues of the Fokker–Planck operator $A^T$. The absolute values of these eigenvalues are connected to the inverse relaxation times of the system. The longest relaxation time has been identified in [37] with the switching time between the two equilibrium states degenerate due to time-reversal invariance. Since then, many papers concentrated on the discussion of the spectral properties of the Fokker–Planck operator; see the review [217] for details.

Although the identification of the eigenvalues of the Fokker–Planck operator with switching times is a plausible assumption, the two quantities do not coincide exactly in the microscopic description. This problem is alleviated in the so-called mean first passage time method[218], where the expectation value of the switching time is calculated directly. The switching time is nothing else than a random variable measuring the time between initializing a system in a part of the phase space and reaching another domain which is disjoint from the original one, corresponding to some neighbourhood of the two considered energy minima. Following the definition in appendix C.1, such a random variable corresponds to a stopping time, and one can use Dynkin’s formula (C.11) to calculate its value.

In the following, we will denote the phase space by $\Omega$ and the target domain by $\Omega_f$, with the initial value of the process outside the target, $x \notin \Omega_f$. If the phase space is infinite or singular at some points, it is necessary to introduce another finite volume $\Omega_b$ which we want to confine the process to, with $\Omega_f \subset \Omega_b$, $x \in \Omega_b$.

We will define the stopping time $\tau$ as the time when the system first reaches the boundary of the target domain $\partial \Omega_f$, or it first tries to leave the simulation area at $\partial \Omega_b$. $\tau$ can be determined by solving the boundary value problem

$$ Af(y) = -1 \text{ for } y \in \Omega_b \setminus \Omega_f, \quad (C.17) $$

$$ f(y) = 0 \text{ for } y \in \partial \Omega_b, \quad (C.18) $$

$$ f(y) = 0 \text{ for } y \in \partial \Omega_f. \quad (C.19) $$

Substituting (C.17)-(C.19) into (C.11) leads to

$$ E^x (f(X_\tau)) = f(x) + E^x \left( \int_0^\tau Af(x_s) \, ds \right) $$

$$ 0 = f(x) - E^x (\tau), \quad (C.20) $$

where the left-hand side is zero since at time $\tau$, the process has reached the boundary with $f(y) = 0$. This demonstrates that $f(x)$ corresponds exactly to the expectation value of $\tau$; the only problem is that we do not know yet whether the system has reached
\partial \Omega_b \text{ or } \partial \Omega_f \text{ first. For deciding this, one has to solve the auxiliary problem}

\begin{align}
A g(y) &= 0 \text{ for } y \in \Omega_b \setminus \Omega_f, \\
g(y) &= 0 \text{ for } y \in \partial \Omega_b \setminus \partial \Omega_f, \\
g(y) &= 1 \text{ for } y \in \partial \Omega_f,
\end{align}

which leads to

\begin{align}
\mathbb{E}^x (g(X_T)) &= g(x) + \mathbb{E}^x \left( \int_0^T A g(X_s) \, ds \right) \\
\mathbb{P}^x (X_T \in \partial \Omega_f) &= g(x).
\end{align}

This means that \( g(x) \) corresponds to the probability of reaching \( \partial \Omega_f \) before \( \partial \Omega_b \). Calculating the switching time reduces to making sure that \( \Omega_b \) is chosen such a way that the system practically never reaches its boundary from a given starting point, which mathematically corresponds to \( g(x) \to 1 \). With such a choice for \( \Omega_b \), solving (C.17)–(C.19) will yield the expected time to reach the neighbourhood of the other equilibrium state \( \Omega_f \). This method is also discussed in the handbooks [216, 219].

For the present case we will consider only a single spin or magnetic particle, described by the cylindrically symmetric Hamiltonian \( H = H(S^z) \). As an example, one can think of the usual uniaxial anisotropy

\[ H = K^{zz} (S^z)^2. \]

By rewriting \( S^z = \cos \vartheta \), the generator of the stochastic process (C.9) simplifies to

\[ A = \left[ -\alpha \gamma' B^{\text{eff},z} \sin \vartheta \frac{\partial}{\partial \vartheta} + 2D \gamma^2 (1 + \alpha^2) \left( \frac{\partial^2}{\partial \vartheta^2} + \cot \vartheta \frac{\partial}{\partial \vartheta} \right) \right] \\
= \left\{ -\alpha \gamma' \frac{1}{M} \frac{\partial H}{\partial S^z} (1 - (S^z)^2) \frac{\partial}{\partial S^z} + 2D \gamma^2 (1 + \alpha^2) \cdot \left[ (1 - (S^z)^2) \frac{\partial^2}{(\partial S^z)^2} - 2S^z \frac{\partial}{\partial S^z} \right] \right\}, \]

so (C.17) and (C.21) transform into ordinary differential equations. Inserting the expression for \( D \) (5.18) into (C.26) leads to

\[ A = \alpha \gamma' \frac{1}{M} \left\{ \frac{\partial H}{\partial S^z} (1 - (S^z)^2) \frac{\partial}{\partial S^z} + k_B T \left[ (1 - (S^z)^2) \frac{\partial^2}{(\partial S^z)^2} - 2S^z \frac{\partial}{\partial S^z} \right] \right\}.\]

The phase space of a single particle corresponds to the unit sphere \( \Omega = S^2 \), simplifying to the interval \( \Omega = [-1, 1] \) for the single variable \( S^z \). We will suppose that the Hamiltonian \( H \) has two minima at \( S^z = 1 \) and \( S^z = -1 \) – see (C.25) for \( K^{zz} < 0 \) –, and we shall describe the transition from the first minimum to the second. The process is started from a point \( S^z \), and will stop when the system has reached the neighbourhood of the second minimum, \( \Omega_f = [-1, b) \). The minimum point \(-1\) is excluded from the domain of the boundary-value problem because the differential operator \( A \) (C.27) is singular at \( S^z = \pm 1 \). Therefore, one also has to exclude the other pole by introducing \( \Omega_b = [-1, a] \) with \( b < S^z < a \), but make sure that the starting point \( S^z \) and \( a \) are sufficiently close to 1. Furthermore, it only makes sense to calculate the time of reaching a subset of finite
measure in the continuous phase space, instead of expecting the process to hit a single point.

The solutions of the differential equations (C.21)-(C.23) and (C.17)-(C.19) are given by

\[
g(S^z) = 1 - \int_b^a e^{\frac{1}{\alpha \gamma T} H(S''')} \frac{1}{1 - (S'')} dS'' \left[ \int_b^a e^{\frac{1}{\alpha \gamma T} H(S''')} \frac{1}{1 - (S'')} dS'' \right]^{-1} \tag{C.28}
\]

\[
f(S^z) = -\int_b^a \int_b^a \frac{M}{\alpha \gamma k_B T} e^{\frac{1}{\alpha \gamma T} H(S''')} \frac{1}{1 - (S'')} \left[ \int_b^a e^{\frac{1}{\alpha \gamma T} H(S''')} \frac{1}{1 - (S'')} dS'' \right]^{-1} dS'' dS’' \tag{C.29}
\]

\[
\times \int_b^a \int_b^a \frac{M}{\alpha \gamma k_B T} e^{\frac{1}{\alpha \gamma T} H(S''')} \frac{1}{1 - (S'')} \left[ \int_b^a e^{\frac{1}{\alpha \gamma T} H(S''')} \frac{1}{1 - (S'')} dS'' \right]^{-1} dS'' dS’'.
\]

If \( H \) is bounded, it can be shown that the limit \( a \rightarrow 1 \) in (C.28)-(C.29) will also lead to bounded functions. For the first case, this yields

\[
g(S^z) \xrightarrow{a \rightarrow 1} \begin{cases} 1 & \text{if } b \leq S^z < 1, \\ 0 & \text{if } S^z = 1, \end{cases} \tag{C.30}
\]

meaning that the system will always reach the vicinity of the second energy minimum before the singular point \( S^z = 1 \) that has zero measure. Equation (C.29) converges to

\[
f(S^z) \xrightarrow{a \rightarrow 1} \frac{M}{\alpha \gamma k_B T} \int_b^a e^{\frac{1}{\alpha \gamma T} H(S''')} \frac{1}{1 - (S'')} \left[ \int_b^a e^{\frac{1}{\alpha \gamma T} H(S''')} \frac{1}{1 - (S'')} dS'' \right]^{-1} dS'' dS’’, \tag{C.31}
\]

corresponding to the switching time when starting the process from \( S^z \). The expression (C.31) has already been derived in [220], where the solution of (C.17)-(C.19) and taking the limit \( a \rightarrow 1 \) was replaced by the boundary condition \( \frac{\partial}{\partial S^z} f = 0 \) for \( S^z = 1 \).

The most important limiting case of (C.31) is obtained when the coefficients in the Hamiltonian are significantly larger than the temperature \( k_B T \). In this case, the system will spend considerable time in the vicinity of the energy minima, and switching events become rare. In this limit, one can replace \( H(S^z) \) with the maximum and minimum values in the positive and negative exponentials, and substitute the integrals with products of the maximum values of the integrands and the width of the exponential function. This leads to the Arrhenius-Néel law (12.7), with the energy barrier

\[
\Delta E = \max_{S^z} H(S^z) - \min_{S^z} H(S^z). \tag{C.32}
\]

It should be mentioned that \( \tau_0 \) in (12.7) also depends on the temperature -- see [37] for a more accurate approximation --, but this dependence is significantly weaker than the exponential term, and can be usually ignored when analysing simulation data. Technically, \( \tau_0 \) and \( \Delta E \) also depend on the initial value of \( S^z \) as well as the stopping point \( b \), but these dependencies can also be omitted if the Hamiltonian takes its minimum and maximum values inside the considered interval \([b, 1]\).

Another limit which can be calculated easily is the case where the temperature is significantly higher than the energy scales in the Hamiltonian. In this case, the exponentials in (C.31) may be replaced by 1 in leading order, and performing the integrals yields

\[
E^x(\tau) = \frac{M}{\alpha \gamma k_B T} \ln \frac{1 + S^z}{1 + b}. \tag{C.33}
\]
This demonstrates that the switching time decays as $1/T$ at high temperatures, since the diffusion coefficient $D$ is proportional to $T$ (5.18), and the distance covered by the diffusion process $x \propto \sqrt{D \tau}$ is fixed. Although the high-temperature limit is generally less useful in applications, it is important when evaluating the simulation methods: while spin dynamics simulations based on the numerical solution of the underlying stochastic differential equation can obviously reproduce this behaviour, Monte Carlo methods where the new value of the spin is chosen uniformly on the whole unit sphere give contradictory results. However, it has been demonstrated in [221] that introducing a temperature-dependent maximal angle with which the spins can be rotated in a single Monte Carlo step fixes this inconsistency; in this case, it is even possible to translate the Monte Carlo step to a real timescale, at least in the limit of high damping parameter $\alpha$.

We have applied the low-temperature limit (12.7) of (C.31) for the description of the skyrmion lifetime in section 11.3 and the switching time of the Co chain in section 12.3. The dependence of the switching time on the Gilbert damping parameter $\alpha$ is illustrated in figure C.1 for the model Hamiltonian used to describe the monatomic Co chain. In agreement with (C.31), we found that only the prefactor $\tau_0$ depends on $\alpha$, but the energy barrier $\Delta E$ does not, since it is determined by the parameters in the Hamiltonian and not the dynamics. As shown in the figure, the power-law dependence $\tau_0 \propto [\alpha/(1+\alpha^2)]^x$ with the exponent $x = -0.93 \pm 0.04$ provides a sufficient description of the simulation results. This is in fairly good agreement with the theoretical prediction for a single spin, which suggests an inverse proportionality between the two quantities. For the skyrmion lifetime, we only performed the simulations for a fixed value of the damping parameter $\alpha = 0.05$, but it was demonstrated in [222] that the dependence on the damping only
affects the prefactor $\tau_0$. In both cases, $\Delta E$ characterizes the interactions in the system, and also provides the strongest temperature dependence due to the exponential form of (12.7).

Finally, we mention that although it is theoretically possible to apply the above procedure to multi-dimensional cases, this causes considerable numerical difficulties. Even for a single particle described by a Hamiltonian that is not axially symmetric, the generally applied method is based on finding the eigenvalues of the Fokker–Planck equation using matrix techniques[217]. For interacting spins, the number of variables in the partial differential equations scales with the number of particles, further complicating the problem.

### C.3 Numerical integration of stochastic differential equations

In this section we will present the mathematical background of the numerical solvers discussed in sections 5.3-5.4, relying on the notations of the handbook [223].

The application of stochastic numerical integration schemes will be illustrated on the one-dimensional Itô diffusion,

\[
\begin{align*}
\text{d}X_t &= a(X_t)\text{d}t + b(X_t)\text{d}W(t) = a(X_t)\text{d}t + b(X_t) \circ \text{d}W(t), \\
X_{t=0} &= X_0, \\
g(X_t) &= a(X_t) - \frac{1}{2}b(X_t)b'(X_t),
\end{align*}
\]

where both the Itô and the equivalent Stratonovich forms are given, and $'$ denotes differentiation with respect to $X_t$.

During the numerical solution, the exact stochastic process $X_t$ is approximated on the interval $[0,T]$ by a process $Y^\delta_t$, which is only defined at certain discrete points in time, and the maximum distance between these discretization steps is $\delta$. Reference [223] describes two types of convergence of $Y^\delta_t$ to the process $X_t$: strong convergence, where $Y^\delta_t$ is pathwise close to $X_t$; and weak convergence, where only the moments of $Y^\delta_t$ converge to $X_t$. An example of weak convergence is when $\Delta W$ – the increment of the Wiener process on a time interval of length $\Delta t$ – is approximated by a random variable $\Delta \overset{\circ}{W}$, which takes the values $\pm \delta$ with probability 0.5, that has the same first and second moments as the Wiener process (C.5)-(C.6). Since in physical problems one is generally interested in expectation values, we will only consider the weak order of convergence. It is said that $Y^\delta_t$ converges weakly to $X_t$ with order $\beta > 0$ if for a certain set of functions $g(X_t)$ there exists a constant $C$ such that

\[
\left| \langle g(X_T) \rangle - \langle g(Y^\delta_T) \rangle \right| \leq C\delta^\beta.
\]

Numerical integration schemes can be constructed by using the Taylor expansion of the exact solution. In case of the Itô form of (C.34), the stochastic Taylor expansion[223]
up to second-order Itô integrals reads

\[ X_t = X_0 + \int_0^t a(X_{t'}) dt' + \int_0^t b(X_{t'}) dW(t'), \quad (C.38) \]

\[ X_t = X_0 + aI_{(0)} + bI_{(1)} + \left( a\dot{a}' + \frac{1}{2} b'' a'' \right) I_{(0,0)} + \ldots, \quad (C.39) \]

where in (C.39) all functions are substituted at their value at the beginning of the interval \( t = 0 \). The multiple Itô integrals on the right-hand side are expressed as

\[ I_{(0)} = \int_0^t dt' = t, \quad (C.40) \]

\[ I_{(1)} = \int_0^t dW(t') = W(t), \quad (C.41) \]

\[ I_{(0,0)} = \int_0^t \int_0^{t'} dt'' dt' = \frac{t^2}{2}, \quad (C.42) \]

\[ I_{(1,1)} = \int_0^t \int_0^{t'} dW(t'') dt'(t') = \frac{W(t)^2}{2} - \frac{t}{2}, \quad (C.43) \]

\[ I_{(0,1)} = \int_0^t \int_0^{t'} dt'' dW(t'), \quad (C.44) \]

\[ I_{(1,0)} = \int_0^t \int_0^{t'} dW(t'') dt'. \quad (C.45) \]

It is easy to check that in the case \( b \equiv 0 \) the expansion coincides with the deterministic Taylor expansion. In order to construct a higher-order numerical scheme, one has to know or at least approximate the derivatives of the \( a \) and \( b \) functions. Due to the stochastic nature of the equation, generally higher-order derivatives are necessary for the same accuracy as in the deterministic case, such as \( a'' \) in the coefficient of \( I_{(0,0)} \). A further problem is that the multiple Itô integrals in (C.40)-(C.45) have to be approximated as well, and most multiple integrals do not even have a closed form – see e.g. \( I_{(0,1)} \) and \( I_{(1,0)} \). Although it is possible to construct a Taylor expansion based on the Stratonovich form of (C.34)[223], the expectation values of multiple Stratonovich integrals are more difficult to calculate, and therefore the order of convergence cannot be determined as easily as in the Itô case. Generally, it is easier to determine the equivalent Itô form of the stochastic differential equation as was done in appendix C.1, and use the Taylor expansion of that form.

To obtain a method with weak order of convergence \( \beta \), basically one has to include all multiple Itô integrals up to order \( \beta \) in the Taylor expansion, and the approximations must reproduce the moments of the exact multiple Itô integrals. For an exact set of sufficient conditions on weak convergence the reader is referred to [223].

In the following, we will only consider \( Y_t^0 \) approximative processes with equidistant time step \( \Delta t \), and denote the value of the process at time \( n\Delta t \) by \( Y_n \). The simplest method with weak order of convergence \( \beta = 1 \) is the stochastic Euler scheme[223],

\[ Y_{n+1} = Y_n + a(Y_n) \dot{I}_{(0)} + b(Y_n) \dot{I}_{(1)}, \quad (C.46) \]
where \( \hat{I}_0 \) and \( \hat{I}_1 \) are the approximations of the Itō integrals (C.40) and (C.41). These integrals fortunately have an exact expression: \( I_0 = \hat{I}_0 = \Delta t \) is a constant, while \( I_1 \) is a Gaussian random variable with mean zero and standard deviation \( \sqrt{\Delta t} \) – see (C.5) and (C.6). This means that \( I_1 \) can be approximated up to arbitrary precision by \( \hat{I}_1 = \sqrt{\Delta t} \xi_n \), where the \( \xi_n \sim \mathcal{N}(0,1) \) are random variables with standard normal distribution which are chosen independently at every time step.

Another simple integration scheme is the stochastic Heun scheme[223],

\[
\tilde{Y}_n = Y_n + \hat{a}(Y_n)\hat{J}_0 + b(Y_n)\hat{J}_1, \quad (C.47)
\]

\[
Y_{n+1} = Y_n + \frac{1}{2} \left( \hat{a}(Y_n) + \hat{a}(\tilde{Y}_n) \right) \hat{J}_0 + \frac{1}{2} \left( b(Y_n) + b(\tilde{Y}_n) \right) \hat{J}_1. \quad (C.48)
\]

Similarly to the deterministic Heun scheme, this is a predictor-corrector method with intermediate step \( \tilde{Y}_n \). Note that this method uses the coefficients from the Stratonovich form of (C.34); to emphasize this, we have denoted the approximations of the stochastic integrals with \( \hat{J}_0, \hat{J}_1 \) instead of the Itō form \( \tilde{I}_0, \tilde{I}_1 \), although these two integrals coincide in Itō and Stratonovich calculus. To obtain convergence, one can use the same approximation of the integrals as in the Euler scheme, \( \hat{J}_0 = \Delta t \) and \( \hat{J}_1 = \sqrt{\Delta t} \xi_n \). Despite the deterministic Heun scheme being a second-order convergent method, the stochastic Heun scheme only has weak order of convergence \( \beta = 1 \) in the general multidimensional case. Due to simply using the coefficients in the Stratonovich form of the differential equation, the higher order of convergence in the deterministic limit and the easy implementation, the stochastic Heun scheme has been used in several numerical implementations of the stochastic Landau–Lifshitz–Gilbert equation[84, 224]. Although higher-order schemes also exist for the solution of stochastic differential equations[223], they generally require the calculation of significantly more terms due to the complicated form of the Taylor expansion (C.39). Therefore, the increase in the applicable time step in higher-order schemes does not always counteract the increase in the computation time of a single step. On the other hand, the improved conservation of properties of the semi-implicit B method in section 5.3 lead to a significant increase in the size of the applicable time step, although without an increase in the order of weak convergence. This is not restricted to the conservation of the length of the spin, which may also be implemented in the Heun scheme by adding a normalization step; this step does not increase its stability considerably.

### C.4 Numerical solvers of the stochastic Landau–Lifshitz–Gilbert equation in the local coordinate system

In this section we will follow the notations of appendix C.3 in presenting the explicit form of the numerical integration methods. As mentioned in section 5.4, all methods presented here have the same order of weak convergence \( \beta = 1 \); the difference is in the stability and the time required for performing a single step.
The two-step scheme (5.32) is given explicitly as

\[
\Delta \tilde{\beta}_{2i} = \frac{\gamma'}{M_i} \frac{\partial E_{\text{band}}}{\partial \beta_{1i}} \tilde{j}_{(0)} - \frac{\alpha}{M_i} \frac{\partial E_{\text{band}}}{\partial \beta_{2i}} \tilde{j}_{(0)} + \gamma' \sqrt{2D_i} e_{2i} \tilde{J}_{(1i)} + \alpha \gamma' \sqrt{2D_i} e_{1i} \tilde{J}_{(1i)},
\]

\[
\Delta \tilde{\beta}_{1i} = - \frac{\gamma'}{M_i} \frac{\partial E_{\text{band}}}{\partial \beta_{2i}} \tilde{j}_{(0)} - \frac{\alpha}{M_i} \frac{\partial E_{\text{band}}}{\partial \beta_{1i}} \tilde{j}_{(0)} + \gamma' \sqrt{2D_i} e_{1i} \tilde{J}_{(1i)} - \alpha \gamma' \sqrt{2D_i} e_{2i} \tilde{J}_{(1i)},
\]

\[
\tilde{S}_i = \left\{ \frac{1}{1-\frac{1}{4} \left( \frac{\Delta \tilde{\beta}_{1i}}{2} \right)^2} \right\} \tilde{S}_i (t_n) + \frac{1}{2} \Delta \tilde{\beta}_{2i} e_{1i} - \frac{1}{2} \Delta \tilde{\beta}_{1i} e_{2i}
\]

\[
\times \left[ 1 + \frac{1}{4} \left( \frac{\Delta \tilde{\beta}_{1i}}{2} \right)^2 \right]^{-1},
\]

\[
\tilde{e}_{2i} = \left\{ \frac{1}{1-\frac{1}{4} \left( \frac{\Delta \tilde{\beta}_{1i}}{2} \right)^2} \right\} e_{2i} + \frac{1}{2} \Delta \tilde{\beta}_{1i} \tilde{S}_i (t_n)
\]

\[
\left[ 1 + \frac{1}{4} \left( \frac{\Delta \tilde{\beta}_{2i}}{2} \right)^2 \right]^{-1},
\]

\[
\tilde{e}_{1i} = \left\{ \frac{1}{1-\frac{1}{4} \left( \frac{\Delta \tilde{\beta}_{2i}}{2} \right)^2} \right\} e_{1i} - \frac{1}{2} \Delta \tilde{\beta}_{2i} \tilde{S}_i (t_n)
\]

\[
\left[ 1 + \frac{1}{4} \left( \frac{\Delta \tilde{\beta}_{2i}}{2} \right)^2 \right]^{-1},
\]

\[
\Delta \beta_{2i} = \frac{\gamma'}{M_i} \frac{\partial E_{\text{band}}}{\partial \beta_{1i}} \hat{j}_{(0)} - \frac{\alpha}{M_i} \frac{\partial E_{\text{band}}}{\partial \beta_{2i}} \hat{j}_{(0)}
\]

\[
+ \gamma' \sqrt{2D_i} \hat{e}_{2i} \hat{J}_{(1i)} + \alpha \gamma' \sqrt{2D_i} \hat{e}_{1i} \hat{J}_{(1i)};
\]

\[
\Delta \beta_{1i} = - \frac{\gamma'}{M_i} \frac{\partial E_{\text{band}}}{\partial \beta_{2i}} \hat{j}_{(0)} - \frac{\alpha}{M_i} \frac{\partial E_{\text{band}}}{\partial \beta_{1i}} \hat{j}_{(0)}
\]

\[
+ \gamma' \sqrt{2D_i} \hat{e}_{1i} \hat{J}_{(1i)} - \alpha \gamma' \sqrt{2D_i} \hat{e}_{2i} \hat{J}_{(1i)};
\]

\[
B_i = - \frac{1}{2} (\Delta \beta_{1i} \hat{e}_{1i} + \Delta \beta_{2i} \hat{e}_{2i}),
\]

\[
A_i = S_i (t_n) + S_i (t_n) \times B_i,
\]

\[
S_i (t_{n+1}) = \frac{A_i + A_i \times B_i + (A_i B_i) B_i}{1 + B_i},
\]

where (5.58) conserves the length of the spins and gives an explicit expression for \( S_i \). The approximate Stratonovich integrals are given by \( \hat{j}_{(0)} = \Delta t \) and \( \hat{j}_{(1i)} = \sqrt{\Delta t} \xi_{r,n}^i \), just as in the global coordinate system discussed in section 5.3.
To present the one-step scheme (5.33), we introduce the shorthand notations

\begin{align}
 x_{2i} &= \frac{\gamma' \partial E_{\text{band}}}{M_i \partial \beta_{2i}} - \alpha \frac{\gamma' \partial E_{\text{band}}}{M_i \partial \beta_{2i}}, \\
x_{1i} &= -\frac{\gamma' \partial E_{\text{band}}}{M_i \partial \beta_{2i}} - \alpha \frac{\gamma' \partial E_{\text{band}}}{M_i \partial \beta_{2i}}, \\
x_{2j2i} &= \frac{\gamma' \partial^2 E_{\text{band}}}{M_i \partial \beta_{2j} \partial \beta_{1i}} - \alpha \frac{\gamma' \partial^2 E_{\text{band}}}{M_i \partial \beta_{2j} \partial \beta_{1i}}, \\
x_{1j2i} &= \frac{\gamma' \partial^2 E_{\text{band}}}{M_i \partial \beta_{1j} \partial \beta_{1i}} - \alpha \frac{\gamma' \partial^2 E_{\text{band}}}{M_i \partial \beta_{1j} \partial \beta_{1i}}, \\
x_{2jii} &= -\frac{\gamma' \partial^2 E_{\text{band}}}{M_i \partial \beta_{2j} \partial \beta_{1i}} - \alpha \frac{\gamma' \partial^2 E_{\text{band}}}{M_i \partial \beta_{2j} \partial \beta_{1i}}, \\
x_{1jii} &= -\frac{\gamma' \partial^2 E_{\text{band}}}{M_i \partial \beta_{1j} \partial \beta_{2i}} - \alpha \frac{\gamma' \partial^2 E_{\text{band}}}{M_i \partial \beta_{1j} \partial \beta_{2i}}, \\
\end{align}

and the approximate Stratonovich integrals

\begin{align}
 \hat{J}_{(0)} &= \Delta t, \\
 \hat{J}_{(1i)} &= \sqrt{\Delta t} \xi_{1i}^\alpha, \\
 \hat{J}_{(0,0)} &= \frac{\Delta t^2}{2}, \\
 \hat{J}_{(1i,1i)} &= \Delta t \left( \xi_{1i}^\alpha \right)^2, \\
 \hat{J}_{(0,1i)} &= \frac{1}{2} \Delta t \left( \xi_{1i}^\alpha - \frac{1}{\sqrt{3}} \xi_{2i}^\alpha \right), \\
 \hat{J}_{(1i,0)} &= \frac{1}{2} \Delta t \left( \xi_{1i}^\alpha + \frac{1}{\sqrt{3}} \xi_{2i}^\alpha \right), \\
 \hat{J}_{(1i,1i)}^{\alpha \beta} &= \frac{1}{2} \Delta t \left( \xi_{1i}^\alpha \xi_{1i}^\beta + \xi_{3i}^\alpha \xi_{3i}^\beta \right) \quad \text{for } \alpha > \beta, \\
 \hat{J}_{(1i,1i)}^{\beta \alpha} &= \frac{1}{2} \Delta t \left( \xi_{1i}^\beta \xi_{1i}^\alpha - \xi_{3i}^\alpha \xi_{3i}^\beta \right) \quad \text{for } \alpha > \beta, \\
\end{align}

where the \( \xi_{1i}^\alpha, \xi_{2i}^\alpha \) and \( \xi_{3i}^\alpha \) are standard normally distributed random variables, which are independent for different indices 1, 2, 3, lattice points \( i \), Cartesian components \( \alpha \) and time steps \( n \). Expressions (5.69)-(5.76) approximate the Itô integrals (5.40)-(5.45) with the same indices, except for \( \hat{J}_{(1i,1i)}^{(0)} \) which is an approximation for \( J_{(1i,1i)}^{(0)} = I_{(1i,1i)}^{(0)} + \frac{1}{2} I_{(0)} \).

With the above notations, the one-step numerical scheme for equations (5.27)-(5.28)
is expressed as

\[
\Delta \beta_{2i} = x_{2i} \dot{J}_{(0)} + \sum_{\alpha} s_{2i}^\alpha \dot{J}_{(1i)} + \frac{1}{2} \sum_{j} (x_{2j} x_{2j i} + x_{1j} x_{1j i}) \dot{J}_{(0,0)}
\]

\[
+ \frac{1}{2} \sum_{j, \alpha} (s_{2j}^\alpha x_{2j i} + s_{1j}^\alpha x_{1j i}) \dot{J}_{(1,0)} + \sum_{\alpha} (x_{2i} s_{2i}^\alpha + x_{1i} s_{1i}^\alpha) \dot{J}_{(0,0)}
\]

\[
+ \frac{1}{2} \sum_{\alpha, \beta} (s_{2i}^\alpha s_{2i}^\beta + s_{1i}^\alpha s_{1i}^\beta) \dot{J}_{(1,1)}^\beta \quad \text{(C.77)}
\]

\[
\Delta \beta_{1i} = x_{1i} \dot{J}_{(0)} + \sum_{\alpha} s_{1i}^\alpha \dot{J}_{(1i)} + \frac{1}{2} \sum_{j} (x_{2j} x_{2j i} + x_{1j} x_{1j i}) \dot{J}_{(0,0)}
\]

\[
+ \frac{1}{2} \sum_{j, \alpha} (s_{2j}^\alpha x_{2j i} + s_{1j}^\alpha x_{1j i}) \dot{J}_{(1,0)} + \sum_{\alpha} (x_{2i} s_{2i}^\alpha + x_{1i} s_{1i}^\alpha) \dot{J}_{(0,0)}
\]

\[
+ \frac{1}{2} \sum_{\alpha, \beta} (s_{2i}^\alpha s_{2i}^\beta + s_{1i}^\alpha s_{1i}^\beta) \dot{J}_{(1,1)}^\beta \quad \text{(C.78)}
\]

\[
S_i(t_{n+1}) = \left\{ \left( 1 - \frac{1}{4} \Delta \beta_{2i}^2 - \frac{1}{4} \Delta \beta_{1i}^2 \right) S_i(t_n) + \Delta \beta_{2i} e_{1i} - \Delta \beta_{1i} e_{2i} \right\}
\]

\[
\times \left[ 1 + \frac{1}{4} \Delta \beta_{2i}^2 \right]^{-1} \quad \text{(C.79)}
\]

Finally, the simplified one-step scheme (5.34) reads

\[
\Delta \beta_{2i} = \frac{\gamma'}{M_i} \frac{\partial E_{\text{band}}}{\partial \beta_{2i}} \dot{J}_{(0)} - \alpha \frac{\gamma'}{M_i} \frac{\partial E_{\text{band}}}{\partial \beta_{2i}} \dot{J}_{(0)}
\]

\[
+ \gamma' \sqrt{2D_i} e_{2i} \dot{J}_{(1i)} + \alpha' \gamma' \sqrt{2D_i} e_{1i} \dot{J}_{(1i)} \quad \text{(C.80)}
\]

\[
\Delta \beta_{1i} = - \frac{\gamma'}{M_i} \frac{\partial E_{\text{band}}}{\partial \beta_{2i}} \dot{J}_{(0)} - \alpha' \frac{\gamma'}{M_i} \frac{\partial E_{\text{band}}}{\partial \beta_{2i}} \dot{J}_{(0)}
\]

\[
+ \gamma' \sqrt{2D_i} e_{1i} \dot{J}_{(1i)} - \alpha' \gamma' \sqrt{2D_i} e_{2i} \dot{J}_{(1i)} \quad \text{(C.81)}
\]

\[
S_i(t_{n+1}) = \left\{ \left( 1 - \frac{1}{4} \Delta \beta_{2i}^2 - \frac{1}{4} \Delta \beta_{1i}^2 \right) S_i(t_n) + \Delta \beta_{2i} e_{1i} - \Delta \beta_{1i} e_{2i} \right\}
\]

\[
\times \left[ 1 + \frac{1}{4} \Delta \beta_{2i}^2 \right]^{-1} \quad \text{(C.82)}
\]

The approximate Stratonovich integrals \( \dot{J}_{(0)} \) and \( \dot{J}_{(1i)} \) are given by (C.69) and (C.70) as before. This method more closely resembles the Euler scheme (C.46), except for the fact that (C.82) ensures that the spins remain normalized, and that the method remains convergent despite using the coefficients in the Stratonovich form of the stochastic differential equation (5.27)-(5.28).

### C.5 Determining the error of cluster spin dynamics simulations

This method was used in section 12.1 to determine the maximal time step applicable in the simulations. When testing the numerical schemes discussed in section 5.4, we
could not assume in advance that the averaging over the simulation data reproduces the expectation value of a physical quantity \( X \) under all circumstances. In this case, it is necessary to determine a confidence interval around the empirical average. For the physical quantity \( X \), the averaging over \( n \) realizations is performed as

\[
X_{\text{avg}} = \frac{1}{n} \sum_{i} X_i, \quad \text{(C.83)}
\]

with \( X_i, i = 1, \ldots, n \) the values of \( X \) at the end of simulations performed with different seed values. The empirical variance of the data is

\[
\text{Var}(X) = \frac{1}{n-1} \sum_{i} (X_i - X_{\text{avg}})^2. \quad \text{(C.84)}
\]

If \( n \) is sufficiently large, it can be assumed that \( X_{\text{avg}} \) is of Gaussian distribution with variance \( \frac{1}{n} \text{Var}(X) \). In this case, the expectation value \( \langle X \rangle \) of the random variable \( X \) falls into a confidence interval around \( X_{\text{avg}} \),

\[
\langle X \rangle \in \left( X_{\text{avg}} - 1.96 \sqrt{\frac{1}{n} \text{Var}(X)}, X_{\text{avg}} + 1.96 \sqrt{\frac{1}{n} \text{Var}(X)} \right), \quad \text{(C.85)}
\]

with probability 0.95. If it is possible to determine \( \langle X \rangle \) on theoretical grounds, and it falls into this confidence interval, then the applied numerical method should reproduce the thermal behaviour of the system correctly. If the analytical value of \( \langle X \rangle \) is outside the interval, then the proposed numerical method is probably inconsistent.
Appendix D

System-specific algorithms

D.1 Details of *ab initio* calculations performed for Fe monolayer on W(110) and Ta(110), as well as for Fe double-layer on W(110)

In this section we will discuss the numerical details of determining the coupling coefficients presented in sections 9.1 and 10.1. We calculated the self-consistent potential of bulk systems using the experimentally determined lattice constants, \(a_W = 3.165\text{Å}\) for W and \(a_{\text{Ta}} = 3.301\text{Å}\) for Ta. In angular momentum indices we have used the cutoff \(l_{\text{max}} = 2\). For the monolayers, we treated a system consisting of eight substrate layers, one layer of Fe and three layers of vacuum, for a total of twelve layers grown on the (110) surface of the bcc lattice. For the double-layer, the top substrate layer was also replaced by Fe. The system was divided into four principal layers, each consisting of 3 atomic layers, covered with semi-infinite substrate from one side and semi-infinite vacuum from the other side, and the potential was determined by the screened Korringa–Kohn–Rostoker method. As discussed in sections 9.1 and 10.1, we have performed the calculations for different relaxation values between the topmost substrate layer and the neighbouring Fe layer.

The spin and orbital magnetic moments obtained from the *ab initio* calculations are listed in table D.1. The sum of the spin and orbital moments in the Fe monolayer on W(110) for 13% inward relaxation compares within 10% to the total magnetic moments given in the literature[131–133]. The induced moments in the topmost W layer are antiparallel to the Fe moments, in agreement with [131, 132], but they are parallel in the next two W layers. It is worth noting that the spin and orbital moments are parallel for the W atoms despite the fact that the W d shell is less than half-filled; this indicates a violation of Hund’s third rule, cf. [132]. The same antiparallel orientation of the Fe and topmost W layers is found in the double-layer, but here the spin and orbital moments are also antiparallel. The two Fe layers are ferromagnetically aligned, in agreement with the experiments. It is notable that the induced moment in the top W layer as well as the moment in the neighbouring Fe layer does not change considerably when the second layer of Fe is added to the system. For Ta substrate, the induced spin magnetic moments are antiparallel to the Fe moments in the top three layers. Hund’s third rule holds in this case, although it must be noted that Ta has one less electron than W, and is thus further away from half-filling where the sign change in Hund’s third rule takes place. Our calculations agree with the results of [133] regarding the fact that increasing the relaxation decreases
<table>
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<th>relaxation</th>
<th>Fe/W(110)</th>
<th>orbital moment ($\mu_B$)</th>
<th>Fe/W(110)</th>
<th>orbital moment ($\mu_B$)</th>
<th>Fe/W(110)</th>
<th>orbital moment ($\mu_B$)</th>
<th>Fe/W(110)</th>
<th>orbital moment ($\mu_B$)</th>
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</thead>
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<td>W1</td>
<td>W2</td>
<td>W3</td>
<td>Fe1</td>
<td>W1</td>
<td>W2</td>
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<td>0.007</td>
<td>0.003</td>
<td>0.180</td>
<td>-0.027</td>
<td>0.001</td>
<td>-0.001</td>
</tr>
<tr>
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<td>0.003</td>
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<td>-0.018</td>
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<tr>
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<td>2.181</td>
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<td>0.017</td>
<td>0.004</td>
<td>0.162</td>
<td>-0.014</td>
<td>0.007</td>
<td>0.001</td>
</tr>
<tr>
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<td>2.122</td>
<td>-0.156</td>
<td>0.022</td>
<td>0.004</td>
<td>0.156</td>
<td>-0.011</td>
<td>0.010</td>
<td>0.002</td>
</tr>
</tbody>
</table>

Table D.1: Calculated spin and orbital moments in the top four layers for Fe monolayer and double-layer on W(110) surface, as well as for Fe monolayer on Ta(110) surface, for selected values of the relaxation.

The magnetic moments of the Fe atoms, most likely due to the increased hybridisation between the Fe layer and the substrate.

The $J_{ij}^{\alpha\beta}$ exchange interactions were determined by supposing ferromagnetic spin configurations within the layers along the [110], [001] and [110] directions. As discussed in appendix A.9, these three directions are sufficient to reproduce the $C_{2\nu}$ symmetry of the surface in the Hamiltonian (3.1). To perform the necessary integrations, 16 energy points were considered along a semicircle contour in the upper complex semiplane, and from 204 up to 6653 $k$ points were sampled in the Brillouin zone, gradually increasing for energies approaching the Fermi level. The exchange interactions were calculated within a circle of radius $8\sqrt{2}\alpha_{W/Ta}$, meaning a total of 562 neighbours in the layer and another 562 neighbours in the other magnetic layer in the double-layer case. When we have included the magnetostatic dipolar interaction in the Monte Carlo simulations in section 9.2, we have chosen the same real-space cutoff as for the exchange interactions.

The antiferromagnetic alignment between the Fe moments and the induced moments in the substrate layers was taken into account in the potential. In the case of the monolayer, we determined the exchange interactions between the induced moments in the top
layer and the Fe moments, and found that they do not change the energy of the system considerably. Therefore, we neglected them in the spin dynamics calculations, and only considered the stable Fe magnetic moments. However, (3.1) with fixed spin lengths probably does not give a good description of the induced moments, because it is expected that their magnitude also depends on the local spin configuration. This means that the model Hamiltonian is only applicable as long as the energy contribution of the induced moments is negligible, which was confirmed by the ab initio calculations for the systems in question.

D.2 Direction of the Dzyaloshinsky–Moriya vectors on bcc (110) surfaces

In this section we will discuss how the $C_{2v}$ symmetry of the lattice influences the direction of the Dzyaloshinsky–Moriya vectors calculated in sections 9.1 and 10.1, illustrated in figures 9.3, 9.4 and 10.2. The out-of-plane component $D_{ij}^z$ disappears between spins in the same layer, since the system has a twofold rotational symmetry around an axis perpendicular to the plane going through the middle point of the line connecting any two lattice points $i$ and $j$ in the layer. This operation switches the two spins and the sign of the $x$ and $y$ spin components, inducing the $J_{ij}^{xy} = J_{ij}^{xy}$ symmetry of the exchange tensors[53]. On the other hand, $D_{ij}^z$ may be finite between spins in different layers as shown in figure 9.4(d).

The components of the Dzyaloshinsky–Moriya vectors are only depicted for neighbours with $R_{ij}^z = R_{ij}^x - R_{ij}^y \geq 0$ and $R_{ij}^0 = R_{ij}^0 - R_{ij}^y \geq 0$ in the figures. The components for the symmetry-related neighbours can be obtained by the following relations: $(−D_{ij}^x, D_{ij}^y)$ for $(R_{ij}^x, −R_{ij}^y)$, $(D_{ij}^x, −D_{ij}^y)$ for $(−R_{ij}^x, R_{ij}^y)$ and $(−D_{ij}^x, −D_{ij}^y)$ for $(−R_{ij}^x, −R_{ij}^y)$. Therefore, $D_{ij}^x$ is only finite between atoms which have a finite distance along the $y$ direction; for example, the atoms at $\sqrt{2} a_{\text{W}}/a_{\text{Wb}}$ distance are located along the $x$ axis, implying $D_{ij}^y = 0$. Similarly, $D_{ij}^y$ is only finite for $R_{ij}^x \neq 0$. $D_{ij}^x$ changes sign when $R_{ij}^x$ or $R_{ij}^y$ is switched to negative, as can be proven using the mirror symmetries of the surface. This also means that $D_{ij}^x$ changes sign when the layer indices 1 and 2 are interchanged and the $R_{ij}^x > 0$, $R_{ij}^y > 0$ convention is kept, while $D_{ij}^x$ and $D_{ij}^y$ do not.

D.3 Mean-field approximation of the parameter range for the transition from the ferromagnetic state to the spin spiral state in the perpendicular plane

The parameter range where a transition described in section 9.3 occurs may be approximated similarly to how it was done in the case of the ferromagnetic reorientation transition in appendix B.3. Instead of considering different magnetization values for every spin in the chain, we will show that the self-consistency equation (4.19) may be fulfilled by only two parameters,

\begin{align}
\langle S_i^x \rangle &= \langle S_x \rangle, \\
\langle S_i^y \rangle &= \sin (k_0^x R_i^x) \langle S_{k_0^x} \rangle, \\
\langle S_i^z \rangle &= \cos (k_0^x R_i^x) \langle S_{k_0^x} \rangle,
\end{align}

(110)
Analogously, in appendix B.3 we only considered such magnetization configurations which were independent from the lattice point. The fact that (D.1)-(D.3) provides a solution to the nonlinear equation (4.19) does not rule out the possibility of further solutions, but the numerical calculations also converged to solutions of the form (D.1)-(D.3), despite considering site-dependent magnetization values.

Substituting the assumptions (D.1)-(D.3) and the considered parameters of the Hamiltonian into (4.19) leads to

\[
\langle S_i^\sigma \rangle = \int S_i^\sigma e^{-\frac{H_{i,MF}}{\beta a^2}} dS_i \left( \int e^{-\frac{H_{i,MF}}{\beta a^2}} dS_i \right)^{-1}, \tag{D.4}
\]

\[
H_{i,MF} = 4J \langle S_i^x \rangle S_i^x + \sum_{(j)} J \langle S_{kj}^y \rangle \left( S_i^y \sin (k_0^y R_j^y) + S_i^z \cos (k_0^y R_j^y) \right) + \sum_{(j)} D_{ij} \langle S_{kj}^y \rangle \left( S_i^y \cos (k_0^y R_j^y) - S_i^x \sin (k_0^y R_j^y) \right) + K_{i}^{xx} (S_i^x)^2. \tag{D.5}
\]

Introducing the local coordinates

\[
\tilde{S}_i^x = S_i^x, \tag{D.6}
\]

\[
\tilde{S}_i^y = \cos (k_0^y R_j^y) S_i^y - \sin (k_0^y R_j^y) S_i^z, \tag{D.7}
\]

\[
\tilde{S}_i^z = \sin (k_0^y R_j^y) S_i^y + \cos (k_0^y R_j^y) S_i^z \tag{D.8}
\]

transforms the mean-field Hamiltonian (D.5) into

\[
\tilde{H}_{MF} = 4J \langle S_i^x \rangle \tilde{S}_i^x + 4J \cos \left( \frac{1}{2} \theta k_0^x \right) \langle S_{kj}^y \rangle \tilde{S}_i^z - 2D \sin (\theta k_0^y) \langle S_{kj}^y \rangle \tilde{S}_i^z + K_{i}^{xx} \left( \tilde{S}_i^x \right)^2, \tag{D.9}
\]

where the \(i\) subscript can be dropped, since the expression no longer depends on the lattice point, just in the notation of the integration variable. Substituting (D.6)-(D.9) into (D.4) confirms the original assumptions (D.1)-(D.3) with the magnetization values given by

\[
\langle S^x \rangle = \int \tilde{S}_i^x e^{-\frac{\tilde{H}_{MF}}{\beta a^2}} dS_i \left( \int e^{-\frac{\tilde{H}_{MF}}{\beta a^2}} dS_i \right)^{-1}, \tag{D.10}
\]

\[
\langle S_{kj}^y \rangle = \int \tilde{S}_i^y e^{-\frac{\tilde{H}_{MF}}{\beta a^2}} dS_i \left( \int e^{-\frac{\tilde{H}_{MF}}{\beta a^2}} dS_i \right)^{-1}. \tag{D.11}
\]

The presence of the reorientation transition can be proven by expanding the free energy (4.18) in the small magnetization values close to the paramagnetic state. In this case we have

\[
\frac{2}{N} F_{MF} \approx -4J \langle S^x \rangle^2 - \frac{1}{k_B T} (4J)^2 \langle S^x \rangle^2 \int \langle S_1^x \rangle^2 e^{-\frac{1}{\beta a^2} K^{xx} (S_1^x)^2} dS_i \times \left( \int e^{-\frac{1}{\beta a^2} K^{xx} (S_1^x)^2} dS_i \right)^{-1} - \left( 4J \cos \left( \frac{1}{2} \theta k_0^x \right) - 2D \sin (\theta k_0^y) \right) \langle S_{kj}^y \rangle^2
\]

\[
- \frac{1}{k_B T} \left( 4J \cos \left( \frac{1}{2} \theta k_0^x \right) - 2D \sin (\theta k_0^y) \right)^2 \langle S_{kj}^y \rangle^2 \int \langle S_1^x \rangle^2 e^{-\frac{1}{\beta a^2} K^{xx} (S_1^x)^2} dS_i \times \left( \int e^{-\frac{1}{\beta a^2} K^{xx} (S_1^x)^2} dS_i \right)^{-1}. \tag{D.12}
\]
Expanding the integrals appearing in (D.12) in $K^{zz}/k_B T$ leads to the stability criteria of the paramagnetic state,

$$ k_B T > -\frac{1}{3} 4J - \frac{4}{15} K^{zz} $$  \hspace{1cm} (D.13) \\

with respect to the ferromagnetic state and

$$ k_B T > -\frac{1}{3} \left( 4J \cos \left( \frac{1}{2} a k_0^y \right) - 2D \sin (a k_0^y) \right) + \frac{2}{15} K^{zz} $$ \hspace{1cm} (D.14)

with respect to the spin spiral state.

The reorientation transition occurs if the paramagnetic state first becomes unstable towards the spiral state,

$$ -4J + 4J \cos \left( \frac{1}{2} a k_0^y \right) - 2D \sin (a k_0^y) - \frac{6}{5} K^{zz} < 0, \hspace{1cm} \text{(D.15)} $$

but the ground state is still ferromagnetic,

$$ -4J + 4J \cos \left( \frac{1}{2} a k_0^y \right) - 2D \sin (a k_0^y) - 2K^{zz} > 0, \hspace{1cm} \text{(D.16)} $$

where the latter condition has been derived in section 6.2. Note that we have considered different values of the spin spiral wave vector $k_0$, but observed that the free energy is minimal for the wave vector minimizing the energy expression (6.6), and the reorientation happens into this spiral state.

### D.4 Equilibrium spin configuration in the SS I state

The equilibrium state in the SS I phase from the model Hamiltonian discussed in section 10.3 may be obtained by a faster numerical procedure than the solution of the relaxation part of the Landau–Lifshitz–Gilbert equation in appendix B.5. We will rely on the fact that only nearest-neighbour exchange interactions $J_1$ and $D$ in figure 10.7 are required for the description of such a state. Equation (B.65) simplifies to

$$ 0 = 2J_1 \left[ \sin (\vartheta_i - \vartheta_{i+1}) + \sin (\vartheta_i - \vartheta_{i-1}) \right] - 2D \left[ \cos (\vartheta_i - \vartheta_{i+1}) - \cos (\vartheta_i - \vartheta_{i-1}) \right] $$
$$ + 2K^{xx} \sin \vartheta_i \cos \vartheta_i. \hspace{1cm} \text{(D.17)}$$

Equation (D.17) can be solved numerically in the case of periodic boundary conditions using the following procedure. The angle $\vartheta_1 = 0$ is fixed, and we take an arbitrary initial value for $\vartheta_2$. All the other angles $\vartheta_i, i = 3, \ldots, L_x$, can be determined from the expression

$$ \vartheta_{i+1} = \vartheta_i + \varphi + \arcsin \left[ \sin (\vartheta_i - \vartheta_{i-1} - \varphi) - \frac{K^{xx} \sin \vartheta_i \cos \vartheta_i}{\sqrt{J_1^2 + D^2}} \right], \hspace{1cm} \text{(D.18)} $$

where the principal value of arcsin should be taken and $\varphi \in [-\pi, \pi]$ is defined as

$$ \cos \varphi = \frac{-J_1}{\sqrt{J_1^2 + D^2}}, \hspace{1cm} \text{(D.19)} $$

$$ \sin \varphi = \frac{D}{\sqrt{J_1^2 + D^2}}. \hspace{1cm} \text{(D.20)} $$
Due to the periodic boundary conditions, (D.18) will also give an approximation for \( \vartheta_1 \) from the angles \( \vartheta_{L_x-1} \) and \( \vartheta_{L_x} \), which new value we will denote by \( \vartheta'_1 \). The angle \( \vartheta_2 \) must be adjusted and the calculation cycle repeated until \( \vartheta'_1 = n2\pi \) is reached within numerical accuracy, where \( n \) is an integer corresponding to the number of wavelengths of the spin spiral state within the periodic simulation cell. The appropriate spiral states can be found by this method from \( n = 0 \), corresponding to the ferromagnetic state, to \( n = L_x/2 \), describing antiferromagnetic ordering. In the spiral state, the torque (D.17) acting on the first spin will also disappear if the angles have the symmetry \( \vartheta_i = \vartheta_{L_x+1-i} \). Note that this torque does not automatically disappear since during the calculation of \( \vartheta_3, \ldots, \vartheta_{L_x} \) and \( \vartheta'_1 \), only the torque conditions (D.17) for spins \( i = 2, \ldots, L_x \) were used.

For free boundary conditions, (D.17) is replaced by

\[
0 = 2J_1 \sin(\vartheta_1 - \vartheta_2) - 2D \cos(\vartheta_1 - \vartheta_2) + 2K^{zz} \sin \vartheta_1 \cos \vartheta_1, \tag{D.21}
\]

\[
0 = 2J_1 \left[ \sin(\vartheta_i - \vartheta_{i+1}) + \sin(\vartheta_i - \vartheta_{i-1}) \right] - 2D \left[ \cos(\vartheta_i - \vartheta_{i+1}) - \cos(\vartheta_i - \vartheta_{i-1}) \right]
+ 2K^{zz} \sin \vartheta_i \cos \vartheta_i \quad \text{for } i = 2, \ldots, L_x - 1, \tag{D.22}
\]

\[
0 = 2J_1 \sin(\vartheta_{L_x} - \vartheta_{L_x-1}) + 2D \cos(\vartheta_{L_x} - \vartheta_{L_x-1}) + 2K^{zz} \sin \vartheta_{L_x} \cos \vartheta_{L_x}. \tag{D.23}
\]

This system of nonlinear equations may be solved by choosing an initial value for \( \vartheta_1 \) and calculating all the other angles. An equilibrium solution is found if for a given \( \vartheta_1 \), the torque acting on the last spin (D.23) disappears. This method, although without the Dzyaloshinsky-Moriya interaction, was developed and described in detail in [225]. However, the solution requires very high numerical accuracy, since many different kinds of equilibrium states may be found for very close values of \( \vartheta_1 \). Some of these equilibrium states will not represent a local energy minimum, because the torque terms (D.21)-(D.23) also disappear around saddle points or energy maxima. However, the spin wave frequencies will only take nonnegative real values around stable equilibrium states, representing local energy minima – see section 4.2.

### D.5 Determining the skyrmion lifetime

To determine the lifetime of skyrmions in section 11.3, we followed the time evolution of the topological charge during the spin dynamics simulations, illustrated in figure D.1. Since \( Q \) is calculated for the complete lattice, the lifetime can only be obtained under some simplifying assumptions. Firstly, we suppose that the increase and decrease of \( Q \) is only due to the creation and annihilation of downwards pointing skyrmions, while the presence of upwards pointing skyrmions or antiskyrmions is excluded. This is largely justified at \( B = 2 \) T by energy considerations given in section 6.4. Even if such structures with opposite topological charge would form in the system, we expect that the energy barrier between the field-polarized state and the skyrmion will mainly depend on the scalar Heisenberg exchange interactions in the system [105, 183], which makes no difference between skyrmions and antiskyrmions with opposite topological charges.

Secondly, it is impossible to directly follow the creation and annihilation of a single skyrmion if only the net topological charge is calculated. As a first approximation, we may assume that the time evolution of the skyrmion density per spin \( n_{sk} \) follows the master equation

\[
\frac{dn_{sk}}{dt} = \frac{1}{\tau_{cr}} - n_{sk} \frac{1}{\tau_{sk}}, \tag{D.24}
\]

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Figure D.1: Sample run for determining the skyrmion lifetime, displaying the topological number $Q$ as a function of time. The parameters are $B = 2\, T$, $T = 110\, K$ and $N = 128 \times 128$.

Figure D.2: Distribution of time $t$ elapsed between skyrmion creation events. The time unit is $t_0 = \frac{\hbar}{2\pi a_{\text{B}}^2} = 2.42 \cdot 10^{-14}\, \text{s}$. As indicated by the fit, the elapsed time follows exponential distribution $e^{-\frac{t}{\tau}}$. The parameters are $B = 2\, T$, $T = 135\, K$ and $N = 64 \times 64$. 
where $1/\tau_{cr}$ is the creation rate of skyrmions due to thermal fluctuations and $\tau_{sk}$ is the skyrmion lifetime. In the stationary case, (D.24) simplifies to

$$\tau_{sk} = \tau_{cr} \langle n_{sk} \rangle,$$  \hspace{1cm} (D.25)

where $\tau_{cr}$ and $\langle n_{sk} \rangle$ are directly measurable by calculating the average time between skyrmion creation events and the average skyrmion number, respectively. We note that none of the parameters in (D.25) depends on the lattice size. During the simulations, it is possible to calculate the average number of skyrmions instead of the density, which is expected to scale linearly with the number of spins $N$. However, the average time between skyrmion creation events is inversely proportional to $N$, because the temperature uniformly excites the spins in the simulated area. Indeed, we found that $\tau_{sk}$ calculated as the product of the average time between skyrmion creation events and the average skyrmion number was the same within statistical error for the lattice sizes $N = 128 \times 128$ and $N = 64 \times 64$.

We note that although the topological charge is quantized, the inflation and shrinking of the skyrmion core is not instantaneous but follows a certain time evolution[222], similarly to the formation and absorption of bubbles in boiling liquids. Therefore, it is unlikely that the skyrmion lifetime, corresponding to the time difference between the creation and annihilation of the same skyrmion, follows exponential distribution, which is generally used to describe the distribution of instantaneous events such as the detection of particles in a detector or scattering in a solid. This suggests that (D.24) may not provide a correct description of the considered dynamical system, since master equations are constructed for continuous-time Markov processes where it is assumed that all creation and annihilation events follow exponential distribution. On the other hand, the skyrmion creation events – the jumps in $Q(t)$ – are instantaneous, meaning that they likely follow a homogeneous Poisson point process. The distribution between neighbouring points in the Poisson process is exponential, and figure D.2 indicates that the average time between skyrmion creation events is in agreement with this distribution.

Instead, it may be preferable to model the skyrmion creation and annihilation events by an M/G/$\infty$ queueing process[226], where it is supposed that the creation process is Markovian, but the elapsed time between the creation and annihilation may follow an arbitrary general distribution. Fortunately, the connection between the expectation values in (D.25) remains true for such a process as will be demonstrated below, and (D.25) is sufficient for the calculation of the average lifetime.

At a fixed point in time, the average density of skyrmions in the system is determined by how many skyrmions were created before, and how many of them are still in the system. The number of created skyrmions in an interval of length $dt$ is simply $dt/\tau_{cr}$, given by a homogeneous Poisson point process. The skyrmions are still in the system if the random variable $\tau$ describing their individual lifetime is larger than the time that has passed since their creation. Since the skyrmions are supposed to be independent, this leads to

$$\langle n_{sk} \rangle = \int_0^\infty Pr(\tau > t) \frac{1}{\tau_{cr}} dt,$$  \hspace{1cm} (D.26)

after integration over all the skyrmions that have been created since the start of the process, supposed to be infinitely long ago in the stationary state. We will assume that $\tau$ has a probability density function $f$; then the probability that the skyrmion is still in
the system after time $t$ is simply

$$\Pr(\tau > t) = \int_t^\infty f(t') dt'.$$  \hfill (D.27)

Inserting (D.27) into (D.26) yields

$$\langle n_{sk} \rangle = \frac{1}{\tau_{cr}} \int_0^\infty \int_0^\infty f(t') dt' = \frac{1}{\tau_{cr}} \int_0^\infty \int_{t'}^\infty f(t') dt d t' = \frac{1}{\tau_{cr}} \int_0^\infty t' f(t') dt',$$  \hfill (D.28)

where the integral on the right-hand side is the expectation value of $\tau$, which was denoted by $\tau_{sk}$ in (D.25).

## D.6 One-dimensional Heisenberg chain

In this section we will derive the analytical expressions for the energy (12.2) and the magnetization (12.5) of the Heisenberg spin chain discussed in section 12.1. Following [201], the first step is determining the partition function of the system,

$$Z = \int e^{-\frac{1}{k_B T} H} \prod_{i=1}^N d S_i,$$  \hfill (D.29)

which can be given in a closed form. Instead of performing the integrals in (D.29) in a global coordinate system, we can change variables in such a way that at every site $i > 1$, the local $z$ axis of the coordinate system is parallel to the previous spin in the chain $S_{i-1}$. This means that we can replace the scalar product $S_{i-1} S_i$ in the Hamiltonian (12.1) by $\cos \vartheta_i$. In this case, (D.29) can be written as a product of integrals over the unit spheres,

$$Z = \int d S_1 \prod_{i=2}^N \int_{-1}^1 2 \pi e^{-\frac{1}{k_B T} \cos \vartheta_i} d \cos \vartheta_i.$$  \hfill (D.30)

As has been demonstrated for the mean-field model in section 4.3, such types of integrals are significantly easier to calculate than multi-dimensional ones. The result is

$$Z = (4\pi)^N \left( \frac{k_B T}{J} \sinh \frac{J}{k_B T} \right)^{N-1},$$  \hfill (D.31)

and (12.2) may be obtained by the well-known expression

$$\langle E \rangle (T) = -\frac{\partial Z}{\partial (k_B T)^{-1}}.$$  \hfill (D.32)

For calculating the squared magnetization, one has to express the expectation value in (12.4) as

$$\langle S_i S_j \rangle = 3 \langle S_i^z S_j^z \rangle = 3 \frac{1}{Z} \int \cos \theta_i \cos \theta_j e^{-\frac{1}{k_B T} H} \prod_{k=1}^N d S_k,$$  \hfill (D.33)

where $\theta_i$ and $\theta_j$ denote angles of the spins with respect to the global $z$ axis. Without loss of generality, we may assume $i \leq j$. In this case, the integrals for $k < i$ and $k > j$ may be
performed by introducing the local coordinates discussed above. On the remaining sites, we must also take into account the orientation of the global $z$ axis besides the direction of the neighbouring spin when changing the integration variables. We define the local coordinate system at site $j$ such a way that the azimuthal angle $\varphi_j$ is measured from the plane spanned by $S_{j-1}$ and the global $z$ direction. Once again, the local polar angle $\vartheta_j$ will be measured from $S_{j-1}$, yielding $\vartheta_j = \theta_j - \theta_{j-1}$. The global $z$ component of $S_j$ may be expressed as

$$
\cos \theta_j = \cos \theta_{j-1} \cos \vartheta_j - \sin \theta_{j-1} \sin \vartheta_j \cos \varphi_j.
$$

and the integral over $S_j$ can be performed in the local coordinate system, yielding

$$
\frac{J}{k_B T} \left( \sinh \frac{J}{k_B T} \right)^{-1} \frac{1}{2} \int_{-1}^{1} \cos \vartheta_j e^{-\frac{J}{k_B T} \cos \vartheta_j} \cos \vartheta_j = -L \left( \frac{J}{k_B T} \right),
$$

with the Langevin function (12.3). The integral over $\cos \varphi_j$ in (D.34) gives zero. We note that (D.35) corresponds to the expectation value of a spin in an effective magnetic field $MB^{z_{\text{eff}}} = -J$, and therefore it coincides with the expectation value calculated in mean-field theory[227].

The change of variables (D.34) has shifted the spin written in the global coordinate system from site $j$ to site $j-1$, which is one step closer to site $i$. Repeating the above procedure, the two spins can formally be moved to the same lattice site, where the normalization $S_i^z = 1$ turns the calculation of the last integral trivial. This leads to the expression

$$
\langle S_i S_j \rangle = \left( -L \left( \frac{J}{k_B T} \right) \right)^{|j-i|}.
$$

Substituting (D.36) into (12.4) and performing the finite summations yields the final result (12.5).
Bibliography


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