

Spin-Spin Correlations in the $\text{CuAlCr}_4\text{S}_8$ Breathing Pyrochlore

by

Itamar Aharony

A thesis
presented to the University of Waterloo
in fulfillment of the
thesis requirement for the degree of
Master of Science
in
Physics

Waterloo, Ontario, Canada, 2023

© Itamar Aharony 2023

Author's Declaration

This thesis consists of material all of which I authored or co-authored: see Statement of Contributions included in the thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

I understand that my thesis may be made electronically available to the public.

Statement of Contributions

Density functional theory (DFT) data provided by Harald O. Jeschke, Okayama University. The DFT data is presented in Table 1.1 in Chapter 1, Table 2.1 in Chapter 2, and Table 3.1 in Chapter 3.

Pseudo-fermion functional renormalization group (PFFRG) data plots are provided by Vincent Nocolak and Johannes Reuther, Freie Universität Berlin in Fig. 3.12, Chapter 3. Pseudo-Majorana functional renormalization group (PMFRG) data plots are provided by Nils Niggemann and Johannes Reuther, Freie Universität Berlin in Fig. 3.13, Chapter 3.

Experimental data shown in Fig. 3.14 and Fig. 5.2 was provided by Sudarshan Sharma, Evan M Smith and Graeme Luke, McMaster University, and Dr. Pascal Manuel, ISIS Pulsed Neutron and Muon Facility, STFC Rutherford Appleton Laboratory.

Code for Monte Carlo was adapted from code that was provided by Daniel Lozano-Gómez. Results of the adapted Monte Carlo code are presented in Chapter 4.

Abstract

Frustrated magnetic systems, whose behaviour is influenced by competing interactions between magnetic spins, have been an active area of research. There is a special class of materials called breathing pyrochlores, whose key difference from “regular” pyrochlores is the breaking of inversion symmetry. Copper-Aluminum-Chromium-Sulfide ($\text{CuAlCr}_4\text{S}_8$) is a candidate for displaying a frustrated Heisenberg model on the breathing pyrochlore lattice. There are two models used for $\text{CuAlCr}_4\text{S}_8$, the Heisenberg model that goes up to third-nearest neighbours (up-to-3rd-NN), and Heisenberg model that goes up to fifth-nearest neighbours (up-to-5th-NN). Both models have exchange couplings obtained from our collaborators using density-functional theory (DFT). Both Heisenberg models for $\text{CuAlCr}_4\text{S}_8$ have exchange couplings that are strongest between third-nearest neighbours, as opposed to more typical pyrochlores that possess stronger exchange couplings between first-nearest neighbours. The peculiarity of the Heisenberg models for $\text{CuAlCr}_4\text{S}_8$, combined with the emerging experimental data, makes it an ideal target for theoretical research. Individual’s methods for theoretical analysis are classical methods, which are mean-field-theory (MFT), large- N , and classical Monte Carlo (CMC) simulation. Collaborators’ methods for theoretical analysis are quantum methods, which are pseudo-fermion functional renormalization group (PFFRG) and pseudo-Majorana functional renormalization group (PMFRG). For the up-to-3rd-NN model, individual’s and collaborators’ results show peaks in the structure factor that are situated on the line $\frac{2\pi}{a}(\pm 1, h, 0)$ up to permutation of the coordinates, for some parameter h , and cubic supercell length a . MFT and large- N suggest peaks at $h = 0$, with a continuous decrease in the structure factor for h away from 0. Monte Carlo shows sharp Bragg peaks at $h = 0$ and $h = \pm 1$. Both of our collaborators’ quantum methods, PFFRG and PMFRG, give peaks at $0 < |h| < 1$, for a seemingly incommensurate h , considering the available wavevector resolution. For the up-to-5th-NN model, individual’s classical methods all give Bragg peaks at $h = 0$ and $h = \pm 1$, while we are awaiting our collaborators’ quantum methods for this model. The magnetic peaks in the experimental data disagree with the expected results from all the classical methods that use the models provided by DFT. We test the possibility of the experimental peaks being the peaks seen in the quantum methods for the up-to-3rd-NN model and the peaks seen in classical methods when altering the exchange couplings provided by DFT. We explain possible causes for disagreements among individual’s classical methods, between individual’s methods and our collaborators’ quantum methods, and between theoretical methods and experimental data.

Acknowledgements

I would like to thank all the people who have been there for me. I want to convey my sincere gratitude to my supervisor, Michel J. P. Gingras, for providing me with an enriching opportunity to generate new research, for his helpful referrals to relevant existing knowledge, and for being an overall supportive mentor. I am grateful for my colleagues, who have been excellent guides. I thank Daniel Lozano-Gómez, who eased me into speaking up when I needed help. I thank Alex Hickey, for sharing his acquired experience to help me prepare for the thesis defence. I thank Subhankar Khatua, who has given me plenty of tips on improving my communication. I thank Kai Chung, whose outlook on physics is profound and inspiring. More thanks for the group members and office members who I was fortunate to share time with; Wen Jin, Naman Gupta, and Felipe Gómez-Lozada. I would also like to thank my parents' neighbour in Ottawa, Jay Godse, for discussing physics with me and providing valuable input. Finally, I would like to thank my family and my late dog, Toffee.

Table of Contents

Author's Declaration	ii
Statement of Contributions	iii
Abstract	iv
Acknowledgements	v
List of Figures	x
List of Tables	xix
List of Abbreviations	xx
List of Symbols	xxi
1 Introduction	1
1.1 Introduction to Frustrated Magnetism	2
1.1.1 Most Basic Toy Model	3
1.1.2 Frustration	9
1.2 Lattices	14
1.2.1 Lattice Vectors	15
1.2.2 Face-Centered-Cubic Lattice	18

1.2.3	Regular Pyrochlore	19
1.2.4	Breathing Pyrochlore	20
1.3	Chromium Spinels	21
1.4	Mechanisms Behind Magnetism in Crystals	25
1.4.1	Exchange Interactions	25
1.4.2	Effect of Electronic Structure	29
1.4.3	Dipolar Interactions	31
1.4.4	Biquadratic Interactions	32
1.5	Motivation Behind $\text{CuAlCr}_4\text{S}_8$	35
1.6	Thesis Overview	36
2	Methods	38
2.1	System Measurements	38
2.1.1	Neutron Scattering	38
2.1.2	Specific Heat	43
2.1.3	Susceptibility	44
2.1.4	Spin-Spin Correlations	46
2.1.5	Powder Average	47
2.2	Exchange Coupling Matrix	48
2.3	Mean Field Theory	50
2.3.1	Mean-Field Approximation	50
2.3.2	Momentum Space	54
2.4	Large- N	59
2.4.1	Quadratic Approximation of Free Energy	59
2.4.2	Ground-State Energy	61
2.4.3	Structure Factor	62
2.4.4	Specific Heat	64
2.4.5	Susceptibility	65

2.4.6	Implementation	66
2.5	Monte Carlo	67
2.5.1	Detailed Balance	68
2.5.2	Over-relaxation	69
2.5.3	Adaptive Spin Update	70
2.5.4	Extracting Data	72
2.6	Chapter Summary	75
3	Semi-Analytical Results	76
3.1	Energy Bands	78
3.2	Mean Field Theory	80
3.2.1	Critical Temperature	80
3.2.2	Structure Factor	81
3.3	Large- N	86
3.3.1	Specific Heat and Susceptibility	87
3.3.2	Structure Factor	88
3.4	Chapter Summary	102
4	Numerical Results	103
4.1	Specific Heat	104
4.2	Susceptibility	106
4.2.1	Curie-Weiss Temperature	108
4.3	Structure Factor	109
4.4	Real-Space Spin Configurations	117
4.5	Chapter Summary	121

5	Discussion	122
5.1	Summary of Research	122
5.1.1	Monte Carlo versus Semi-Analytical	122
5.1.2	Classical versus Quantum Semi-Analytical Methods	124
5.1.3	Theoretical versus Experimental Data	125
5.1.4	Insight on Current Results	128
5.2	Outlook for Future Research	129
5.3	Conclusion	130
	References	132
	APPENDICES	142
A	Nearest Neighbours and Adjacency Matrices	143
A.1	Defining Adjacency Matrices	143
A.2	Degeneracy Lines in the up-to-3 rd -NN Model	148
A.2.1	4 th and 5 th Nearest Neighbours	153
B	FCC Results	155
B.1	Classical Monte Carlo	155
B.2	Large- N and Mean-Field Theory	157
B.3	Summary of Appendix B	158

List of Figures

1.1	Up-facing red arrows and down-facing blue arrows represent $\sigma = +1$ and $\sigma = -1$, respectively. a) A one-dimensional chain, where the nearest neighbours of each spins are the closest spins on each side. b) A square lattice, where the spins are located on the vertices of a square mesh. Two spins are nearest neighbours if they are on the same edge of a square grid.	5
1.2	a) Ground state for nearest-neighbour zero-field Ising model on a square-lattice with ferromagnetic coupling ($J < 0$). b) Ground state for same model but with antiferromagnetic coupling ($J > 0$). For the square-lattice nearest-neighbour Ising model, the antiferromagnetic model in Panel b) can be mapped onto a ferromagnetic model by flipping $J \rightarrow -J$ and flipping spins in a checkerboard pattern simultaneously. This ability to map between ferromagnetic and antiferromagnetic models is not guaranteed for systems with different interactions or different geometries, as will be seen in later subsections.	6
1.3	Some arbitrary state for the XY model on a square lattice with nearest-neighbour coupling. The spins are free to be any unit vector in the plane of the lattice.	8
1.4	Ground states of the XY model for a) ferromagnetic nearest-neighbour couplings ($J < 0$), b) antiferromagnetic nearest-neighbour couplings ($J > 0$). .	8
1.5	Assuming antiferromagnetic interactions, spins minimize energy when facing in opposite direction to their neighbours. a) Frustration of Ising spins on a single triangle b) Frustration of Ising spins on a single tetrahedron. For both of these small systems, it is impossible to have each spin point in opposite direction to all its neighbours.	9

1.6	Two of the ground states of the nearest-neighbour antiferromagnetic XY model. The ground states in panels a) and b) represent the two possible chiralities, and any other ground state is related to one of them by global spin rotations. This leads to the phase-space volume of the ground-state manifold being independent of the system size.	11
1.7	Six of the many possible ground states in the antiferromagnetic Ising model on the triangular lattice. The qualification of a ground state in this model is that all spins on each triangular plaquette are either two-up-one-down or two-down-one-up, which can be satisfied by a number of states that grows exponentially with the system size.	13
1.8	Illustration of order by disorder. When there is an accidental degenerate ground state manifold, the system favours a subset of the ground state manifold that allows the most modes of fluctuations. This selection within the subspace about the red dot in the right panel is caused by entropy, which is seen as the driving mechanism for disorder. Thus, the selection mechanism is called “order by disorder” (ObD).	14
1.9	a) Some two-dimensional Bravais lattice b) A non-Bravais lattice with the same underlying primitive translations as the lattice in Panel a)	16
1.10	FCC lattice visualization a) A single cubic unit b) A larger portion of the lattice, with the same cubic units marked for reference. Notice that the lattice sites, marked with gray balls, are located at the corners of the cubes and at the centers of the faces of the cubic units.	19
1.11	a) Regular pyrochlore lattice, with lattice sites at the corners of the tetrahedra. b) Breathing pyrochlore lattice, with alternating tetrahedra sizes. The breathing pyrochlore could also look like Panel a) as long as there is some other property that differentiates between the red and blue tetrahedra, such as having different nearest-neighbour exchange couplings.	21

1.12	Subset of the tetrahedra that form a breathing pyrochlore, where the lattice sites are at the corners of the tetrahedra. Arrows show displacements between small-tetrahedron-edge nearest neighbours (exchange coupling J_{1a}), large-tetrahedron-edge nearest neighbours (exchange coupling J_{1b}), second-nearest neighbours (J_2), direct third-nearest neighbours (J_{3a}), indirect third-nearest neighbours (J_{3b}), fourth-nearest (J_4) and fifth-nearest (J_5) neighbours. Definition of neighbours is the same as the one used for the breathing pyrochlore in Ref. [1], with the labeling difference from there to here being $J \rightarrow J_{1a}$, $J' \rightarrow J_{1b}$. For explicit list of displacement vectors corresponding to each type of neighbour, refer to Appendix A.	23
2.1	Schematic of neutron scattering. A beam of neutrons with wavevector $\mathbf{k}$ is fired at a sample. The neutrons interact with the particles in the lattice via magnetic interactions and get scattered. For a given scattered beam with out-going wavevector $\mathbf{k}'$, the solid angle spanned by the beam depends on several variables, including the magnetic correlations of spins in the sample.	39
2.2	Overrelaxation of a spin in site j , with initial spin $\mathbf{S}_j$ and a local field $\mathbf{h}_j$. The spin vector is rotated around $\mathbf{h}_j$ to update the spin from $\mathbf{S}_j$ to $\mathbf{S}'_j$	70
2.3	Schematic of rotating a spin vector $\mathbf{S}_j$ into a new vector $\mathbf{S}'_j$. a) A random unit vector $\mathbf{u}$ is chosen in the plane orthogonal to $\mathbf{S}_j$. b) An spin update by rotating $\mathbf{S}_j$ around $\mathbf{u}$ to make the spin at site j be $\mathbf{S}'_j$	72
3.1	In the model, the magnetic Cr^{3+} ions are the spins, located at the corners of the tetrahedra. Exact coordinates corresponding to the displacement between each type of neighbours is provided in Appendix A.	77
3.2	Exchange coupling eigenvalue bands for a selected path in the Brillouin zone, for the up-to-3 rd -NN model. The eigenvalues are of the Fourier-transformed exchange coupling matrix, $\mathcal{J}(\mathbf{q})$, defined in Eq. (2.59). Note that the absolute minimum of the lowest eigenvalue is attained along a degeneracy line passing through $\frac{\pi}{a}[0, 2, 0]$ and $\frac{\pi}{a}[2, 2, 0]$. The degeneracy line means that internal energy does not select a single well-defined ordering wavevector, although other phenomena such as ObD may narrow down the set of ordering wavevectors. Since the minima are not at $\mathbf{q} = 0$, this suggests that the ordering of the spin cannot be represented by a single unit cell, since the wavelength of the ordering wavevectors spans multiple unit cells.	79

3.3	Exchange coupling eigenvalue bands for a selected path in the Brillouin zone, for the up-to-5 th -NN model. The minima at the lowest band for wavevectors $\pi/a[0, 2, 0]$ and $\pi/a[2, 2, 0]$ are global minima and thus the classical ordering wavevectors.	80
3.4	Plots of MFT structure factor for CuAlCr ₄ S ₈ model up to J_{3b} , spin modulus $S = 3/2$, the MFT critical temperature is $T_C^{\text{MF}} = 20.475$ K.	82
3.5	Plots of MFT structure factor for the CuAlCr ₄ S ₈ model up to J_5 , spin modulus $S = 3/2$. The MFT critical temperature is $T_C^{\text{MF}} = 33.75$ K.	85
3.6	Large- N analysis for model with exchange couplings up to 3 rd NN. a) Specific heat versus temperature. There is no sign of a phase transition since the heat capacity remains continuous, but the curve does flatten at around $T \approx 10$ K. The absence of a singularity in the heat capacity is due to approximations made in large- N . Large- N also fails to capture a singularity in the specific heat for the ferromagnetic nearest-neighbour simple cubic Heisenberg model (for which there should be a phase transition with an infinite heat capacity [2]). b) Reciprocal susceptibility, with asymptote to the Curie-Weiss temperature, given by Eq. (2.40). The high temperature behaviour agrees with the Curie-Weiss law.	87
3.7	Large- N analysis for model with exchange couplings up to J_5 a) Specific heat. Like Fig. 3.6a), there is no indication of a phase transition in the heat capacity, but a flattening of the curve below a certain temperature. For the up-to-5 th -NN parameters, this flattening takes place at around ≈ 20 K. b) Reciprocal susceptibility, with asymptote to the Curie-Weiss temperature, which is -41.85 K for the specific exchange couplings in the model.	88
3.8	Plots of large- N structure factor with up-to-3 rd -NN exchange coupling at various temperatures.	90
3.9	Powder average of the large- N structure factor for the up-to-3 rd -NN parameters at various temperatures. The peaks, which are sharper at low temperatures, correspond to commensurate wavevectors. The dashed red vertical lines correspond to wavevectors of the form $\frac{\pi}{a}(2h, 2k, 2l)$ for integers h, k, l , which correspond to the wavevector moduli at peaks that we will see in the results from Monte Carlo simulations in Chapter 4.	91
3.10	Plots of large- N structure factor with up-to-5 th -NN exchange coupling at various temperatures.	93

3.11	Powder average of the large- N structure factor for the up-to-5 th -NN parameters at various temperatures. The peaks, which are sharper at low temperatures, are at the same wavevector moduli as the peaks in the powder average for the up-to-3 rd -NN parameters. The dashed red vertical lines correspond to wavevectors of the form $\frac{\pi}{a}(2h, 2k, 2l)$ for integers h, k, l , which correspond to the wavevector moduli at peaks that we will see in the results from Monte Carlo simulations in Chapter 4.	94
3.12	[Used with permission from Vincent Nocolak, Freie Universität Berlin] PFFRG structure factor at $T = 0$ at the $[hk0]$ plane (left panel), and $[hhl]$ plane (right panel). The Hamiltonian is the up-to-3 rd -NN Heisenberg model. The peaks of the structure factor in the $[hk0]$ plane (left panel) are away from but centered at the midpoint of the box edges, and the wavevector of the peaks seem to be correlated at the available resolution. Note the different convention in this plot, where the wavevectors are $\mathbf{q} = \frac{2\pi}{a}(h\hat{x} + k\hat{y} + l\hat{z})$, as opposed to the convention used for the rest of the structure factor plots in this thesis, $\mathbf{q} = \frac{\pi}{a}(h\hat{x} + k\hat{y} + l\hat{z})^1$	96
3.13	[Used with permission from Nils Niggemann, Freie Universität Berlin] PMFRG structure factor at the $[hk0]$ plane at various temperatures, using the up-to-3 rd -NN Heisenberg model. Temperatures are in the unit of $J_{3a} = 6$ K. The units for the wavevectors in this figure are determined by setting $a = 1$ as the cube length in the FCC lattice translation. Similarly to PFFRG, the peaks are on the edges of the boxes and away from the midpoint of the edges. These peaks draw closer together to the midpoints of the box edges at higher temperatures, thus becoming more similar to the classical results.	97
3.14	[Data included with permission from Sudarshan Sharma, McMaster University] Experimental powder average of neutron scattering in $\text{CuAlCr}_4\text{S}_8$. Blue peaks are magnetic peaks that only appear below the critical temperature, while orange peaks are structural peaks that exist due to the structure of the lattice sites rather than the orientation of the spins. Vertical dashed lines are the wavevector moduli that correspond to wavevectors of the form $\frac{\pi}{a}(2h, 2k, 2l)$ for integers h, k, l . Monte Carlo and large- N predict peaks to take place at wavevectors of that form. However, the experimental magnetic peaks disagree with the peaks predicted by large- N (and Monte Carlo simulations, whose structure factor we will see in Chapter 4).	98
3.15	Ordering wavevector classification vs. exchange couplings J_{1b} and J_{3b} . All other up-to- J_3 couplings are fixed to the values given in Table 2.1.	99

3.16	a) Large- N structure factor in $[hk0]$ and $[hhl]$ planes and b) powder average plots with exchange couplings up to J_{3b} with the alteration $J_{3b} : 0.58J_{3a} \rightarrow 0.4J_{3a}$, $J_{1b} : -0.45J_{3a} \rightarrow -0.25J_{3a}$. This set of parameters was chosen since J_{1b} , J_{3a} , and J_{3b} are the three dominant exchange couplings in the up-to-3 rd -NN model and these couplings are expected to change the ordering wavevector according to the phase diagram in Fig. 3.15	100
3.17	a) Large- N structure factor in $[hk0]$ and $[hhl]$ planes and b) powder average plots with exchange couplings up to J_{3b} with the alteration $J_{3b} : 0.58J_{3a} \rightarrow 0.35J_{3a}$, $J_{1b} : -0.45J_{3a} \rightarrow -0.25J_{3a}$. This alteration results in a powder average that has a magnitude below $2\pi/a$, which is a property that is seen for the first peak in the experimental powder average, shown in Fig. 3.14.	101
4.1	$k_B T \chi_{\text{uniform}}/N_s \approx \langle M^2 \rangle/N_s$ vs. number of Monte Carlo sweeps for $\text{CuAlCr}_4\text{S}_8$ Heisenberg model going up to J_{3b} . The system starts at a random spin configuration (as one would expect at $T = \infty$), and is thermalized at temperature 100 K. Each sweep is N_s proposed spin updates. The plot is obtained by averaging over 50,000 independent runs. As can be seen, the systems needs a few dozens of Monte Carlo sweeps to thermalize, after which the system reaches thermal equilibrium.	104
4.2	Specific heat plots for couplings up to J_{3b} , for different linear system sizes L (where there are $L \times L \times L$ unit cells) a) zoomed around the critical temperature b) zoomed out. Note that besides the peak at the critical temperature, no other features were observed at temperature range 0.1-1000 K (the range of the plot is 0.1 K- 100 K, but temperatures up to 1000 K were investigated). The growth in the height of the peaks at $T \approx 9.9(1)$ K as a function of system size suggests that the peaks represent a phase transition.	105
4.3	Specific heat plots for couplings up to J_5 , for different system sizes L (where there are $L \times L \times L$ unit cells) a) zoomed around the critical temperature b) zoomed out. Note that besides the peak at the critical temperature, no other features were observed at temperature range 0.1-1000 K. The growth in the height of the peaks at $T \approx 21.6(1)$ K as a function of system size suggests that the peaks represent a phase transition.	106

4.4	Uniform-field susceptibility at zero field. The uniform-field susceptibility is the derivative of the mean magnetization of the system with respect to the intensity of a uniform field. The classical Curie-Weiss temperature is -37.125 K	107
4.5	Susceptibility vs. temperature for couplings up to J_5 . Curie-Weiss temperature is -41.85 K	107
4.6	Structure factor along the $[hk0]$ plane for system size $28 \times 28 \times 28$ unit cells, when including exchange couplings up to J_{3b} . The wavevector represented by $[hk0]$ is $\mathbf{Q} = \frac{\pi}{a}(h\hat{x} + k\hat{y})$	109
4.7	Structure factor along the $[hhl]$ plane for system size $28 \times 28 \times 28$ unit cells, when including exchange couplings up to J_{3b} . The wavevector represented by $[hhl]$ is $\mathbf{Q} = \frac{\pi}{a}(h\hat{x} + h\hat{y} + l\hat{z})$	110
4.8	Structure factor in the $[hk0]$ plane at temperature $T \sim 10^{-3}T_C$ including couplings up to J_{3b} . Despite the degeneracy line, there are peaks that sharper as the system size increases, suggesting Bragg peaks. These Bragg peaks also happen for the Bravais lattice analogue, the FCC, as discussed in Appendix B.	111
4.9	Structure factor along the $[hk0]$ plane for system size $16 \times 16 \times 16$ unit cells, when including exchange couplings up to J_5 . The wavevector represented by $[hk0]$ is $\mathbf{Q} = \frac{\pi}{a}(h\hat{x} + k\hat{y})$	112
4.10	Structure factor along the $[hhl]$ plane for system size $16 \times 16 \times 16$ unit cells, when including exchange couplings up to J_5 . The wavevector represented by $[hhl]$ is $\mathbf{Q} = \frac{\pi}{a}(h\hat{x} + h\hat{y} + l\hat{z})$	113
4.11	a) Phase diagram from Fig. 3.15, with the parameters for the up-to-3 rd -NN model for $\text{CuAlCr}_4\text{S}_8$ marked as a yellow star $[(J_{3b}/J_{3a}, J_{1b}/J_{3a}) \approx (0.58, -0.45)]$, and the parameters in this figure marked in a gray star $[(J_{3b}/J_{3a}, J_{1b}/J_{3a}) = (0.45, -0.25)]$. b) Monte Carlo and c) large- N structure factor plots for system with $16 \times 16 \times 16$ unit cells at $T = 0.1J_{3a} \approx 0.6$ K.	114
4.12	a) Phase diagram from Fig. 3.15, with the parameters for the up-to-3 rd -NN model for $\text{CuAlCr}_4\text{S}_8$ marked as a yellow star $[(J_{3b}/J_{3a}, J_{1b}/J_{3a}) \approx (0.58, -0.45)]$, and the parameters in this figure marked in a gray star $[(J_{3b}/J_{3a}, J_{1b}/J_{3a}) = (0.4, -0.25)]$. b) Monte Carlo and c) large- N structure factor plots for system with $16 \times 16 \times 16$ unit cells at $T = 0.1J_{3a} \approx 0.6$ K.	115

4.13	a) Phase diagram from Fig. 3.15, with the parameters for the up-to-3 rd -NN model for CuAlCr ₄ S ₈ marked as a yellow star $[(J_{3b}/J_{3a}, J_{1b}/J_{3a}) \approx (0.58, -0.45)]$, and the parameters in this figure marked in a gray star $[(J_{3b}/J_{3a}, J_{1b}/J_{3a}) = (0.35, -0.25)]$. b) Monte Carlo and c) large- N structure factor plots for system with $16 \times 16 \times 16$ unit cells at $T = 0.1J_{3a} \approx 0.6$ K.	116
4.14	a) Phase diagram from Fig. 3.15, with the parameters for the up-to-3 rd -NN model for CuAlCr ₄ S ₈ marked as a yellow star $[(J_{3b}/J_{3a}, J_{1b}/J_{3a}) \approx (0.58, -0.45)]$, and the parameters in this figure marked in a gray star $[(J_{3b}/J_{3a}, J_{1b}/J_{3a}) = (0.3, -0.25)]$. b) Monte Carlo and c) large- N structure factor plots for system with $16 \times 16 \times 16$ unit cells at $T = 0.1J_{3a} \approx 0.6$ K.	117
4.15	Four cubic supercells from four different $16 \times 16 \times 16$ unit cell systems from CMC simulations of the up-to-3 rd -NN model. Each cubic cell is from a different system thermalized at $0.01\text{K} \sim 10^{-3}T_C$. Note that with the exception of the configuration in the top-right, the spins on the corners of the boxes point in different directions, suggesting some contribution from wavevectors that are not $\frac{2\pi}{a}(\pm 1, \pm 1, 0)$ or $\frac{2\pi}{a}(\pm 1, 0, 0)$. As suggested by the structure factors shown in Fig 4.8, the selection of the $\frac{2\pi}{a}(\pm 1, \pm 1, 0)$ or $\frac{2\pi}{a}(\pm 1, 0, 0)$ ordering wavevectors should become more dominant for larger systems. . .	119
4.16	Four cubic supercells from four different $16 \times 16 \times 16$ unit cell systems from CMC simulations of the up-to-5 th -NN model. Each cubic cell is from a different system thermalized at $0.02 \text{ K} \sim 10^{-3}T_C$. Notice how all the spins along the corners of the cubes point in the same direction (up). This suggests that the states are at ordering wavevectors $\mathbf{Q} = \frac{2\pi}{a}(\pm 1, 0, 0)$ or $\mathbf{Q} = \frac{2\pi}{a}(\pm 1, \pm 1, 0)$, with the cubic supercells being repeating units.	120
5.1	Illustration of order-by-disorder within the degeneracy lines that form the ground state manifold in the model using the up-to-3 rd -NN couplings from density-functional theory (DFT). Although a ground state could be represented by any wavevector in the ground-state manifold, thermal fluctuations favour selection within the intersections of the degeneracy line. This order-by-disorder (ObD) selection within the ground state manifold favours states that permit more modes of thermal fluctuations for systems with nonzero temperatures [3].	124

5.2	[Data included with permission from Sudarshan Sharma, McMaster University] Plots of experimental neutron scattering powder average for $\text{CuAlCr}_4\text{S}_8$. The peaks of interest are the blue peaks, which only appear below the critical temperature due to magnetic ordering. a) Experimental powder average compared with vertical dashed lines at the expected locations of peaks of the form $[hh0] + \mathbf{G}$, which are types of peaks seen when altering the exchange parameters in the up-to-3 rd -NN model. b) Same experimental data, with vertical dashed line at peaks of the form $2\pi/a(1, q_k, 0) + \mathbf{G}$, which are the types of peaks seen in our collaborators' PFFRG and PMFRG.	127
A.1	Illustration of types of neighbours on a subset of the breathing pyrochlore, with sites on the corners of the tetrahedra.	145
B.1	Structure factor for FCC lattice from Monte Carlo simulations along the $[hk0]$ plane for $16 \times 16 \times 16$ unit cells. The wavevector represented by $[hk0]$ is $\mathbf{Q} = \frac{\pi}{a}(h\hat{x} + k\hat{y})$	156
B.2	Structure factor for nearest-neighbour AFM Heisenberg model on the FCC lattice from Monte Carlo simulations along the $[hhl]$ plane for $16 \times 16 \times 16$ unit cells. The wavevector represented by $[hhl]$ is $\mathbf{Q} = \frac{\pi}{a}(h\hat{x} + h\hat{y} + l\hat{z})$. . .	157
B.3	Structure factor for nearest-neighbour AFM Heisenberg on the FCC lattice from large- N for $16 \times 16 \times 16$ unit cells. The wavevector represented by $[hk0]$ is $\mathbf{Q} = \frac{\pi}{a}(h\hat{x} + k\hat{y})$, and for $[hhl]$ the wavevector is $\mathbf{Q} = \frac{\pi}{a}(h\hat{x} + h\hat{y} + l\hat{z})$. Note that the wavevectors forms uniform-intensity peaks along the degeneracy lines in the $[hk0]$ plane, in contrast to the discrete peaks seen for the Monte Carlo structure factor in Fig. B.1.	158

List of Tables

1.1	Table of exchange couplings for various chromium spinels, obtained via a method called density-functional theory (DFT). The titular material, $\text{CuAlCr}_4\text{S}_8$, is at the bottom row, marked in red. All entries except for the bottom row are reported in Ref. [4], and the parameters for $\text{CuAlCr}_4\text{S}_8$ were obtained from our collaborators. The dominant third-nearest-neighbour couplings in $\text{CuAlCr}_4\text{S}_8$ are highlighted in blue. The T column is the temperature for which the exchange couplings are derived.	24
2.1	Two sets of exchange parameters, types of neighbours are sketched in Fig. 1.12. The up-to-3 rd -NN parameters are obtained from a DFT fit which assumes that any neighbours further than $3b$ do not interact. The up-to-5 th -NN parameters are fitted with the assumption that interaction are up to fifth-nearest-neighbour.	49
3.1	Table of exchange couplings used in the Heisenberg model for $\text{CuAlCr}_4\text{S}_8$. .	77
4.1	Table containing the mean-field critical temperature, T_C^{MF} , the classical Monte Carlo critical temperature, T_C^{CMC} , and the Curie-Weiss temperature, Θ_{CW} . These temperatures are shown for both the up-to-3 rd -NN and up-to-5 th -NN models, whose exchange couplings are given in Table 3.1.	121

List of Abbreviations

AFM	Antiferromagnetic
BZ	Brillouin Zone
CMC	Classical Monte Carlo
DFT	Density-Functional Theory
FCC	Face-Centered Cubic
FM	Ferromagnetic
MFT	Mean-Field Theory
NN	Nearest Neighbour
ObD	Order by Disorder
PFFRG	Pseudo-Fermion Functional Renormalization Group
PMFRG	Pseudo-Majorana Functional Renormalization Group

List of Symbols

a	Lattice constant; length of cube in FCC lattices
$\mathbf{a}_1, \mathbf{a}_2, \dots$	Primitive lattice translation vectors
$\mathbf{b}_1, \mathbf{b}_2, \dots$	Primitive reciprocal lattice translation vectors
c, d	Sublattice site indices
e	Euler's number (≈ 2.7183)
E	Energy
$\mathcal{H}$	Hamiltonian
I, H	Unit-cell indices
j, j'	Site indices
$\mathcal{J}_{jj'}$	Exchange coupling between spins in sites j and j'
$\mathcal{M}$	Microstate of the system
$\mathbf{s}_j$	Spin vector at site j
$\hat{x}, \hat{y}, \hat{z}$	Cartesian basis vectors
ν, μ	Cartesian component index
π	Pi constant (≈ 3.1416)
λ	Large- N Lagrange-multiplier scalar
ψ	Quantum state

Chapter 1

Introduction

The whole is not always a sum of its parts; for example, the person reading this thesis is alive, but is made of molecules that on their own are inanimate. Water can be liquid or vapour but the molecules that make it up have no concept of “liquid” or “gas” on their own. Lone birds cannot form a flying formation, yet a flock of birds has a shape that spans over multiple birds [5]. The universe consists of many components that have certain behaviours when isolated, but the same components can combine to create systems whose behaviour is completely different. This concept, called emergence, has been the target of human curiosity as far back as at least 2000 years ago [6].

On the physics front, at the turn of the 20th century, physicists were attempting to explain phase transitions in materials such as water. There have been challenges in rigorous mathematical analyses, since a typical macroscopic sample consists of $\sim 10^{23}$ interacting particles, and fully analyzing such a system requires computational power that is beyond attainable [7]. Instead, physicists and mathematicians were looking for possible approximations that can reduce the computational requirements without excessively sacrificing precision. This gave rise to statistical mechanics.

With the advent of statistical mechanics, magnetic systems also gained interest. Magnetic systems have been known by ancient cultures such as ancient Greeks and ancient Chinese [8]. Naturally-occurring minerals, which the Greeks referred to as “lodestone”, and the Chinese referred to as “soft stone”, were noted for their ability to attract some metals. It would not be until two millennia later when scientists discovered the mechanism behind these magnetic systems. With advancements in physics and chemistry, it is now known that magnetic systems consist of magnetic atoms that interact with each other. In a well known magnetic system, the fridge magnets, the interactions between the

constituent magnetic atoms favours a state where their magnetic moments align to create cumulative magnetic moment, hence a macroscopic magnet. The emergent property is the temperature-dependence of the magnet's state; while magnetic atoms are always magnetic no matter the temperature of the sample they constitute, a magnetic system may lose its cumulative magnetic moment above a critical temperature [9]. The mathematical analysis of the emergent properties of magnetic systems has become a major field in statistical mechanics and condensed matter physics.

A special group of materials that consist of interacting magnetic particles are pyrochlores. The name “pyrochlore” comes from Greek $\pi\tilde{\nu}\rho$ (“pyr”) meaning “fire”, and $\chi\lambda\omega\rho\acute{o}\varsigma$ (“chloros”) meaning “green”. The name is as such due to the green fire that appeared when igniting the crystals. The term “pyrochlore lattice” became a term for crystals whose particles are arranged in periodic arrays of corner-sharing tetrahedra, which is described in Section 1.2.

In this thesis, the goal is to predict the magnetic properties of Copper Aluminum Chromium Sulfide ($\text{CuAlCr}_4\text{S}_8$), which is modeled as having magnetic Cr^{3+} ions forming a variation of the pyrochlore lattice, which is explained in Section 1.2.4. The type of interactions between the magnetic Cr^{3+} ions in $\text{CuAlCr}_4\text{S}_8$ has unique properties that are explained later in Sections 1.3 and 1.5. The research of $\text{CuAlCr}_4\text{S}_8$ is motivated by its unique properties combined with the availability of experimental data and several theoretical methods to compare among. This thesis is focused on classical methods used to analyze $\text{CuAlCr}_4\text{S}_8$. The results of classical analyses and their comparison with collaborators' methods should give insight on the reliability of classical methods in analysing microscopic magnetic systems. Given the unique model used to describe $\text{CuAlCr}_4\text{S}_8$, what can classical methods such as mean-field theory, large- N , and classical Monte Carlo simulations predict?

1.1 Introduction to Frustrated Magnetism

Before delving into more specific topics of research, we shall go over simple toy models that pioneered the study of the magnetic systems. Their simplicity made these models targets for some of the first rigorous mathematical analysis of statistical mechanics in interacting systems. We see how a relevant phenomenon, called “magnetic frustration”, can arise in some of the simplest magnetic systems. The main question for frustrated systems is, “what happens to a system if minimizing energy for one interaction costs energy for a different coexisting interaction?” [10].

1.1.1 Most Basic Toy Model

The mathematical model used to denote the interactions between spins in $\text{CuAlCr}_4\text{S}_8$ is an expanded model based on the toy models. For this reason, it is beneficial to look at the thermodynamics of the toy models.

Partition Function

The systems that are studied in this thesis are assumed to be in the canonical ensemble, that is, the system is situated in an environment with a constant temperature, called a “heat bath” [11]. This assumption makes sense in the context of magnetic systems, since we are interested in the temperature dependence of system variables and thus define temperature as a system variable. To describe temperature dependencies in the system, the partition function of the system is a useful function of temperature, defined as

$$\mathcal{Z} = \sum_{\text{states } \mathcal{M}} e^{-\beta \mathcal{H}(\mathcal{M})}, \quad (1.1)$$

where $\beta = 1/(k_{\text{B}}T)$ for temperature T and Boltzmann constant k_{B} . $\mathcal{H}(\mathcal{M})$ is the energy (or Hamiltonian) of the system when it is in the microstate $\mathcal{M}$. The summation in (1.1) is over all possible states in the system. The partition function is useful for determining the probability of a system at inverse-temperature β to be in a given microstate $\mathcal{M}$, which is

$$P(\mathcal{M}) = \frac{e^{-\beta \mathcal{H}(\mathcal{M})}}{\mathcal{Z}}. \quad (1.2)$$

This probability itself is useful as a weight factor when taking the thermally weighted expectation value of observables such as energy, magnetization, etc. For an observable $\mathcal{O}$ with value $\mathcal{O}(\mathcal{M})$ for each microstate $\mathcal{M}$, the thermal expectation value of $\mathcal{O}$ is

$$\langle \mathcal{O} \rangle = \frac{1}{\mathcal{Z}} \sum_{\text{states } \mathcal{M}} \mathcal{O}(\mathcal{M}) e^{-\beta \mathcal{H}(\mathcal{M})}. \quad (1.3)$$

While the temperature-dependence of observables is investigated in the thesis, a crucial part in low-temperature analysis is the ground states. For that case, define the ground-state energy as

$$E_{\text{g.s.}} = \min_{\text{states } \mathcal{M}} \mathcal{H}(\mathcal{M}), \quad (1.4)$$

where the minimum of the Hamiltonian over all possible states is taken. To deal with the zero temperature case, where $\beta \rightarrow \infty$, it is befitting to rewrite Eq. (1.3), as following:

$$\langle \mathcal{O} \rangle = \frac{e^{-\beta E_{\text{g.s.}}} \sum_{\text{states } \mathcal{M}} \mathcal{O}(\mathcal{M}) e^{-\beta[\mathcal{H}(\mathcal{M}) - E_{\text{g.s.}}]}}{e^{-\beta E_{\text{g.s.}}} \sum_{\text{states } \mathcal{M}} e^{-\beta[\mathcal{H}(\mathcal{M}) - E_{\text{g.s.}}]}}. \quad (1.5)$$

Taking the limit $\beta \rightarrow \infty$ in Eq. (1.5) and noting that $\mathcal{H}(\mathcal{M}) \geq E_{\text{g.s.}}$, then only the ground states contribute in the summation, giving

$$\lim_{T \rightarrow 0} \langle \mathcal{O} \rangle = \frac{\sum_{\text{g.s. } \mathcal{M}} \mathcal{O}(\mathcal{M})}{N_{\text{g.s.}}}, \quad (1.6)$$

where $N_{\text{g.s.}}$ is the number of ground states, and the summation in the numerator in Eq. (1.6) is over ground states only. This means that only ground states contribute to the thermal expectation value of observables in the limit of low temperatures.

Ising Model

While the toy models that are shown here have phenomena that were fruitful enough to have their own theses written, only the relevant parts of these models are covered. The most basic magnetic model is the Ising model, introduced by Ernst Ising and his supervisor Wilhelm Lenz in 1925 [12, 13]. The model goes as the following:

$$\mathcal{H} = \sum_{i>j=1}^{N_s} J_{ij} \sigma_i \sigma_j + \sum_{i=1}^{N_s} h_i \sigma_i, \quad \sigma_k \in \{-1, +1\} \quad \forall k = 1, \dots, N_s, \quad (1.7)$$

where σ_i is the spin at site i , J_{ij} is the exchange coupling between the spin at sites i and the spin at site j , h_i is an external magnetic field at site i , and N_s is the number of sites. For convenience, we refer to $\sigma_i = +1$ as “up” and $\sigma_i = -1$ as “down”. One could get a simple version of the Ising model, the nearest-neighbour Ising model, whose Hamiltonian is

$$\mathcal{H} = \sum_{\langle ij \rangle \in \text{N.N.}} J \sigma_i \sigma_j + \sum_i h_i \sigma_i, \quad (1.8)$$

where $\langle ij \rangle \in \text{N.N.}$ means that site i and site j are nearest neighbours. Simple structures on which the spins can reside are the one-dimensional chain and the two-dimensional square lattice (refer to Fig. 1.2 for illustration).

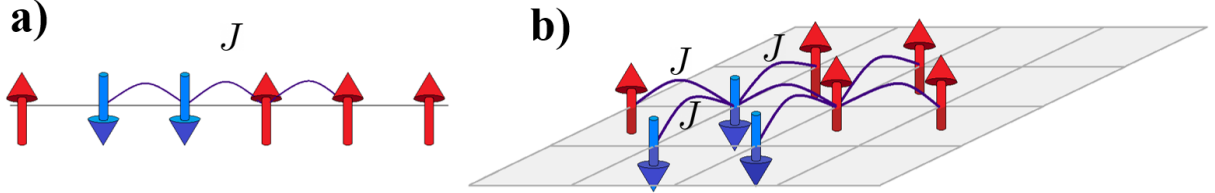


Figure 1.1: Up-facing red arrows and down-facing blue arrows represent $\sigma = +1$ and $\sigma = -1$, respectively. **a)** A one-dimensional chain, where the nearest neighbours of each spins are the closest spins on each side. **b)** A square lattice, where the spins are located on the vertices of a square mesh. Two spins are nearest neighbours if they are on the same edge of a square grid.

The simplicity of the Ising model is that the spins have discrete degrees of freedom by virtue of each spin having only two possible states (“up” and “down”). Even for a system as simple as the Ising model, the number of states grows exponentially as 2^{N_s} , where N_s is the number of sites. Finding the partition function and canonical averages of observables as per Eq. (1.3) can be computationally costly. To give a perspective on how hard it is to obtain a closed form for partition functions for general large systems, Lars Onsager solved in 1944 the nearest-neighbour Ising model on a square lattice [14]. The partition function for the Ising model on a three-dimensional cubic lattice has not been solved exactly to this day. Despite this inconvenience for describing the behaviour of the system at any arbitrary temperature, in the limit of low temperatures, only ground states matter, as shown in Eq. (1.6). For the square lattice, the ground states depend on whether the interaction is ferromagnetic ($J < 0$) or antiferromagnetic ($J > 0$), and are shown in Fig. 1.2.

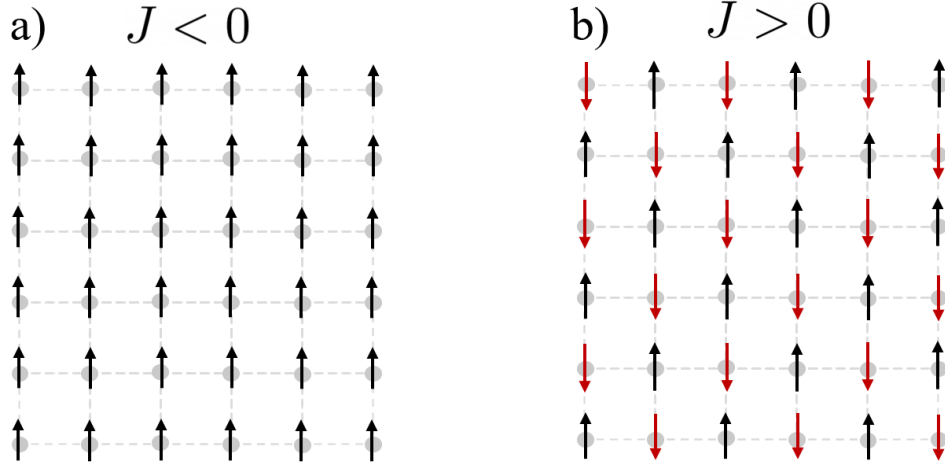


Figure 1.2: **a)** Ground state for nearest-neighbour zero-field Ising model on a square-lattice with ferromagnetic coupling ($J < 0$). **b)** Ground state for same model but with antiferromagnetic coupling ($J > 0$). For the square-lattice nearest-neighbour Ising model, the antiferromagnetic model in Panel **b)** can be mapped onto a ferromagnetic model by flipping $J \rightarrow -J$ and flipping spins in a checkerboard pattern simultaneously. This ability to map between ferromagnetic and antiferromagnetic models is not guaranteed for systems with different interactions or different geometries, as will be seen in later subsections.

For the antiferromagnetic case, Louis Néel calculated that the ground state can be thought of as the two ground states of an Ising ferromagnet with sites interwoven into an alternating pattern, and published his findings in 1952 [15]. This picture has helped in analyzing the antiferromagnetic system in terms of the more familiar ferromagnetic system, but it cannot always be done for other types of antiferromagnetic systems that are shown in following subsections.

***XY* Model**

The *XY* model is analogous to the Ising model but with a higher number of spin components. In the *XY* model, spins are two-dimensional unit vectors, restricted in the x - y

plane, with the following Hamiltonian:

$$\begin{aligned}\mathcal{H} &= \sum_{ij} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j + \sum_i \mathbf{h}_i \cdot \mathbf{S}_i \\ &= \sum_{ij} J_{ij} (s_i^x s_j^x + s_i^y s_j^y) + \sum_i (h_i^x s_i^x + h_i^y s_i^y),\end{aligned}\tag{1.9}$$

where $\mathbf{S}_i = (s_i^x, s_i^y)$ is a unit vector in a two-dimensional plane, and $\mathbf{h}_i = (h_i^x, h_i^y)$ is the external field applied at site i . For the following discussion, unless stated otherwise, assume $\mathbf{h}_i = \mathbf{0} \forall i$. The square-lattice XY model is illustrated in 1.3. Similarly to the Ising model, we focus on the nearest-neighbour case:

$$\mathcal{H} = J \sum_{\langle ij \rangle \in \text{N.N.}} (s_i^x s_j^x + s_i^y s_j^y)\tag{1.10}$$

where the external field is neglected for the chosen model. While the zero-field Ising Hamiltonian from Eq. (1.7) is invariant under global spin flips $\sigma_i \rightarrow -\sigma_i \forall i$, the zero-field XY Hamiltonian in Eq. (1.9) is invariant under global rotation of spins $\mathbf{S}_i \rightarrow \mathcal{R} \mathbf{S}_i \forall i$ for any rotation matrix $\mathcal{R}$ in the x - y plane. That symmetry of the Hamiltonian exists due to the rotational invariance of the dot product. This means that states that are related to each other by global rotation of the spins have the same energy. Aside from the rotational symmetry caused by the additional degrees of freedom in the XY model, the ground states are the same as the square-lattice Ising model, as can be seen in Fig. 1.4. So far, the ground state in the explored models is constructible by naively minimizing the energy between each interacting pair. This triviality in finding the ground state is not guaranteed for other models, which we will see in the next section. The complications that arise are relevant to the main topic of this thesis; the $\text{CuAlCr}_4\text{S}_8$ breathing pyrochlore.

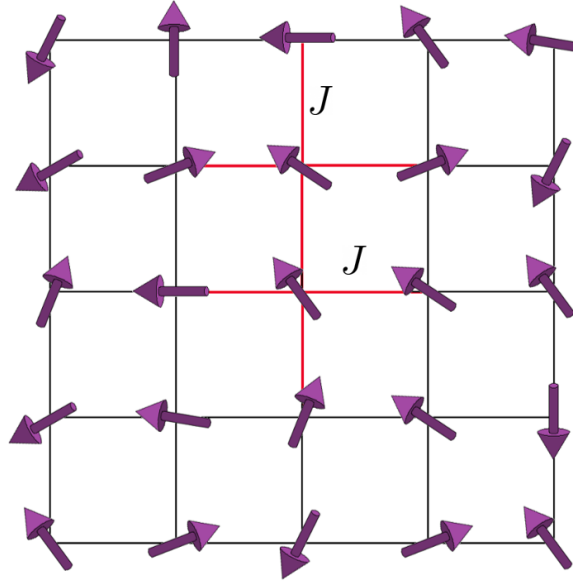


Figure 1.3: Some arbitrary state for the XY model on a square lattice with nearest-neighbour coupling. The spins are free to be any unit vector in the plane of the lattice.

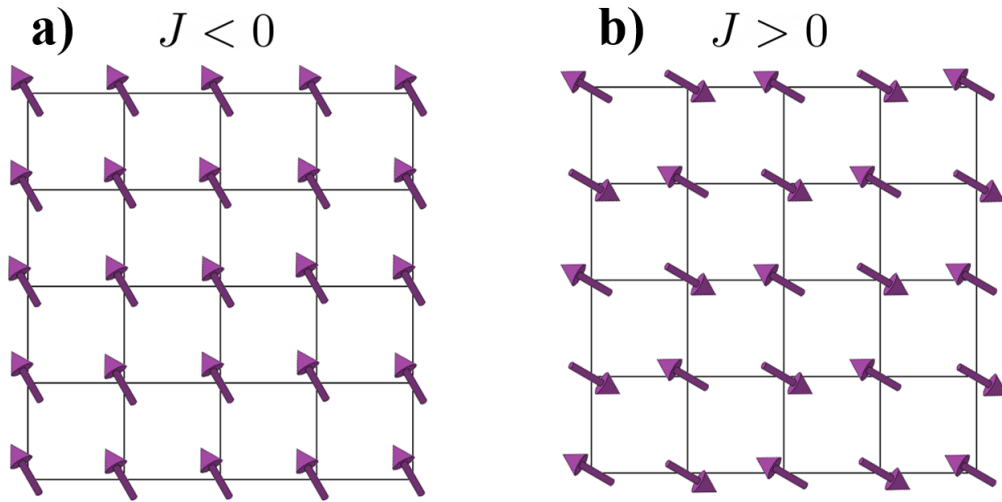


Figure 1.4: Ground states of the XY model for **a)** ferromagnetic nearest-neighbour couplings ($J < 0$), **b)** antiferromagnetic nearest-neighbour couplings ($J > 0$).

1.1.2 Frustration

So far, we discussed models whose ground states involve minimizing the interaction energy between each interacting pair. Frustrated systems, on the other hand, are systems in which the energy cannot be minimized simply by minimizing the energy in each interacting pair; minimizing the energy in one interaction increase the energy for another coexisting interaction. The term “frustration” in magnetic systems was coined in a lecture by Philip Anderson in 1976 [16] and in subsequent papers [17,18]. Even then, frustrated systems were studied before being called by that name back in 1950 [19,20]. In this thesis, the main focus is on geometrically frustrated systems. In geometrically frustrated systems, interactions compete due to the geometry of the system, such as antiferromagnetic interactions on a structure that cannot allow all the spins to point in opposite direction to all of its neighbouring spins. Examples of simple geometrically frustrated systems are shown in Fig. 1.5. As mentioned, antiferromagnetic square-lattice Ising model studied by Louis Néel [15] in 1952. Although that system is not frustrated, his analysis method has been relevant to classifying a system as frustrated. Néel investigated the susceptibility of antiferromagnetic systems and showed a distinction between two temperatures, the critical temperature where phase transition occurs, and the Curie-Weiss temperature, Θ_{CW} , which is the extrapolated ordering temperature from high-temperature susceptibility and may be negative. It is not necessary to reach zero temperature or solve explicitly for the ground states to know whether a system is frustrated, as long as one can show that the system only undergoes a magnetic phase transition at a temperature much lower than $|\Theta_{CW}|$ [10].

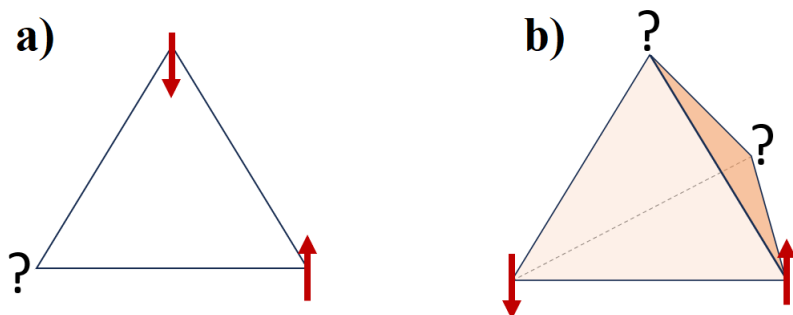


Figure 1.5: Assuming antiferromagnetic interactions, spins minimize energy when facing in opposite direction to their neighbours. **a)** Frustration of Ising spins on a single triangle **b)** Frustration of Ising spins on a single tetrahedron. For both of these small systems, it is impossible to have each spin point in opposite direction to all its neighbours.

Although the frustrated models shown here are antiferromagnetic, couplings do not have to be antiferromagnetic for a system to be frustrated, as some geometries can also cause frustration even in ferromagnetic models. Although such systems are not presented here, there is more information about frustrated ferromagnetism in Ref. [21]. A possible and relevant property of some frustrated systems is their intrinsic ground-state entropy [22].

Small Ground-State Entropy

While the antiferromagnetic ($J > 0$) square-lattice Ising model is not a frustrated system, the triangular lattice XY model, shown in Fig. 1.6, is an example of a frustrated system. The Hamiltonian is the same as Eq. (1.9) (the case where $h_i = 0 \forall i$). The model has a set of exactly solvable ground states. Consider a group of three spins, $\mathbf{S}_i, \mathbf{S}_j, \mathbf{S}_k$. Noting that $\|\mathbf{S}_i\| = \|\mathbf{S}_j\| = \|\mathbf{S}_k\| = 1$ for classical normalized spins, then

$$\|(\mathbf{S}_1 + \mathbf{S}_2 + \mathbf{S}_3)\|^2 = 2(\mathbf{S}_1 \cdot \mathbf{S}_2 + \mathbf{S}_1 \cdot \mathbf{S}_3 + \mathbf{S}_2 \cdot \mathbf{S}_3) + \underbrace{\|\mathbf{S}_1\|^2 + \|\mathbf{S}_2\|^2 + \|\mathbf{S}_3\|^2}_{\text{constant}}, \quad (1.11)$$

which means that the Hamiltonian for nearest-neighbour XY model on the triangular lattice can be rewritten as

$$\mathcal{H} = \frac{J}{2} \sum_{ijk \in \triangle} (\mathbf{S}_i + \mathbf{S}_j + \mathbf{S}_k)^2 + \text{constant}, \quad (1.12)$$

where $ijk \in \triangle$ means that sites i, j, k are vertices of a triangular plaquette. A triangular plaquette is a triangle consisting three spins that are all nearest neighbours of each other. The $1/2$ factor in Eq. (1.12) accounts for double counting since each pair of interacting spins forms an edge that belongs to two triangular plaquettes. From Eq. (1.12), this means that the ground state is $\mathbf{S}_i + \mathbf{S}_j + \mathbf{S}_k = 0 \forall i, j, k$ being vertices of a triangular plaquette. Noting that the spins are two-dimensional vectors, and choosing for instance that $\mathbf{S}_i = \hat{y}$ (parallel to y -direction) to ignore the rotational symmetry, then there are only two possible choices for $\mathbf{S}_j$ and $\mathbf{S}_k$, leading to two possible ground states shown in Fig. 1.6. This remains for the reader as an exercise.

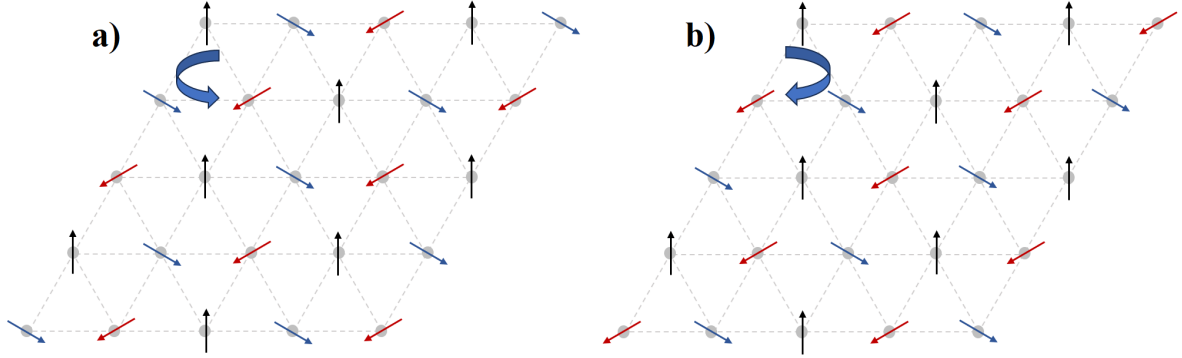


Figure 1.6: Two of the ground states of the nearest-neighbour antiferromagnetic XY model. The ground states in panels **a)** and **b)** represent the two possible chiralities, and any other ground state is related to one of them by global spin rotations. This leads to the phase-space volume of the ground-state manifold being independent of the system size.

While the ground state of the system is exactly solvable, note that no interacting pair of spins has its energy minimized, as it would have been the case only if the spins were anti-parallel. Minimizing the global energy to get the ground state is different from minimizing the energy in each interacting pair, since it is impossible to minimize the energy of all interacting pairs simultaneously. Up to rotations, there are two ground states with different chirality, meaning that all ground states are related to each other by global rotations and reflections of the spins. This property of the set of ground states invites the analysis of the system's entropy, defined as

$$S = k_B \ln \mathcal{W}, \quad (1.13)$$

where k_B is Boltzmann's constant and $\mathcal{W}$ is the volume of accessible phase space. Boltzmann's constant is often dropped in Eq. (1.13) by choosing a unit system where $k_B = 1$. To explain $\mathcal{W}$, one can interpret each state of the system as a point in a multi-dimensional space, where each dimension corresponds to each degree of freedom of the system. $\mathcal{W}$ is the volume (or measure) of the set of states within that space. In the antiferromagnetic nearest-neighbour XY -model on the square lattice, the ground states are all related to each other by rotation, and thus each ground state can be parametrized by a single degree of freedom $\theta \in [0, 2\pi)$. This means that the ground-state manifold, the set of all ground state, is a one-dimensional set with a constant measure, meaning that in the zero-temperature limit, where only ground states are accessible, $\mathcal{W}$ is a constant independent of the system

size. This means that the entropy as defined in Eq. (1.13) is a system-size-independent constant at zero temperature, satisfying the Third Law of thermodynamics [7].

Extensive Ground-State Entropy

While we have shown that the antiferromagnetic nearest-neighbour XY -model on the triangular lattice is a model that obeys the third law of thermodynamics, it is possible for some other frustrated systems to have an extensive ground-state entropy that grows with the size of the system. The entropy of the ground states behaves in such a way when the spins on the same triangular lattice are Ising. The antiferromagnetic Ising system on the triangular lattice is a frustrated system like the analogous XY model, but the results of the frustration are different. The difference lies in the Ising model's inability to access the same ground states that the XY -model has in Fig.1.6. Instead, the Ising model's ground states are any states where each triangular plaquette has a two-up-one-down or a one-up-two-down configuration, as can be seen in Fig.1.7. The number of such ground states depends on the size of the system and grows exponentially with the size of the system. In 1950, Gregory Wannier calculated that the number of ground states for a system with N_s sites is

$$\mathcal{W}_{\text{ground state}}^{\text{Ising, triangular}} \approx e^{0.338N_s}. \quad (1.14)$$

Using Eq. (1.13) with $\mathcal{W} = \mathcal{W}_{\text{ground state}}^{\text{Ising, triangular}}$, the antiferromagnetic nearest-neighbour Ising model on the triangular lattice at zero temperature has an extensive entropy $S(T = 0) \approx 0.338k_B N_s$ [19].

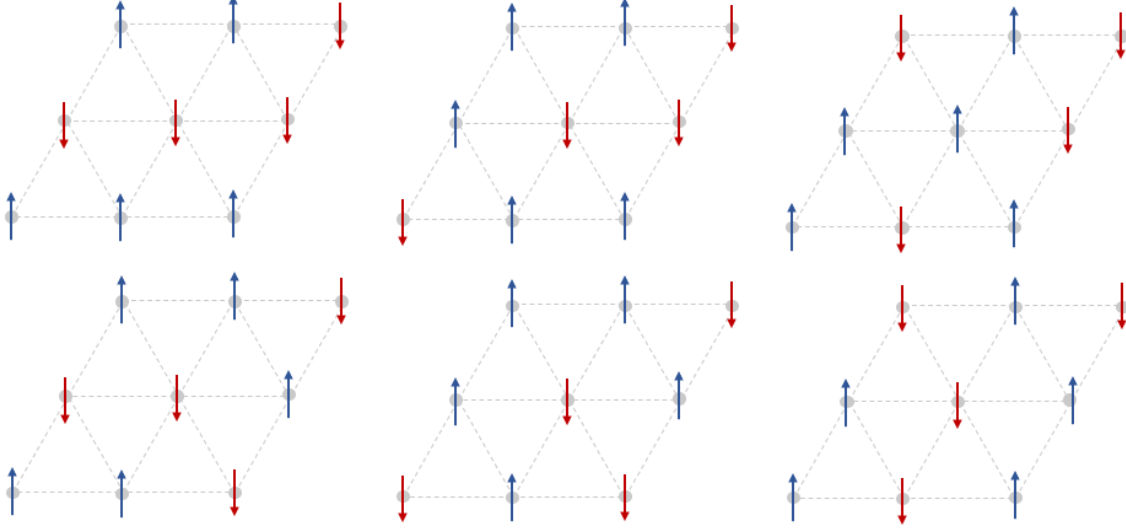


Figure 1.7: Six of the many possible ground states in the antiferromagnetic Ising model on the triangular lattice. The qualification of a ground state in this model is that all spins on each triangular plaquette are either two-up-one-down or two-down-one-up, which can be satisfied by a number of states that grows exponentially with the system size.

While the Ising model on the triangular lattice is a constructed model, extensive ground-state entropy is also applicable in more realistic physical systems. For instance, in 1935, Linus Pauling showed that there is a possible extensive entropy in water ice due to proton positioning about O^{2-} ions under the hydrogen-bond interactions [23, 24].

Selection Within Degenerate Ground State Manifold

In 1973, Anderson proposed that some frustrated systems would behave as “spin liquids”, where the system is resonating between multiple ground states, and the system does not order even at zero temperature [25]. This has been found to be more difficult to achieve practically, since even within the highly-degenerate ground state manifold, some states are favoured due to a phenomenon called order-by-disorder (ObD). In ObD, as systems tend towards maximizing their entropy, having a large degenerate ground-state manifold suggests that there might be some selection mechanism within the manifold [10, 26, 27], as illustrated in Fig. 1.8. ObD maximizes entropy by selecting states that allow for the most

fluctuations around them, which could be thermal fluctuations in the limit of $T \rightarrow 0^+$ or quantum fluctuations at $T = 0$ [3, 28, 29].

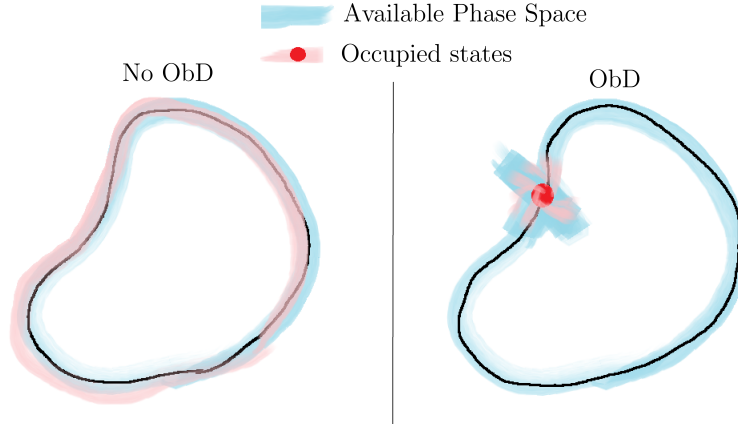


Figure 1.8: Illustration of order by disorder. When there is an accidental degenerate ground state manifold, the system favours a subset of the ground state manifold that allows the most modes of fluctuations. This selection within the subspace about the red dot in the right panel is caused by entropy, which is seen as the driving mechanism for disorder. Thus, the selection mechanism is called “order by disorder” (ObD).

ObD means that having a degenerate ground-state manifold does not guarantee that all ground states are accessed equally, and one should be on the lookout to see how a system behaves if it has a degenerate classical ground-state manifold.

1.2 Lattices

A common type of real frustrated systems are crystals that consist of interacting particles forming periodic structures called lattices. For example, common table salt (sodium chloride) consists of crystals, where each crystal is a periodic array of sodium and chlorine atoms. The lattices’ geometries combined with their prevalence in nature makes them compelling for research. This section goes over the basic concepts of what makes a lattice, and the toolbox for analyzing such materials. A main part of the thesis involves the spin-spin structure factor, which is a quantity that contains information on spin-spin correlations in a lattice.

1.2.1 Lattice Vectors

The following lattice vector definitions are taken from Kittel's *Introduction to Solid-State Physics* [30]. Lattices are structures consisting of a periodic arrangement of atoms. A lattice can be defined by primitive translation vectors $\mathbf{a}_1, \mathbf{a}_2, \dots, \mathbf{a}_d$, where d is the number of spatial dimensions in the lattice. With that definition of the primitive translation vector, then any vector of the form

$$\mathbf{R} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + \dots + n_d \mathbf{a}_d, \quad n_1, n_2, \dots, n_d \in \mathbb{Z} \quad (1.15)$$

is a lattice translation vector. One could define a lattice as the set of all points satisfying Eq. (1.15). Likewise, for any $\mathbf{R}$ satisfying Eq. (1.15), translating any lattice position $\mathbf{r}$ as $\mathbf{r} \rightarrow \mathbf{r} + \mathbf{R}$ should map the lattice onto itself. A crystal consists of a periodic arrangement of atoms that are invariant under translation by lattice vectors, hence there is a discrete translational invariance. In the case of a Bravais lattice, the positions of lattice sites can be fully represented as vectors in Eq. (1.15). Otherwise, a non-Bravais lattice is a collection of more than one but a finite number of atoms, called a basis, that repeats in space by translation vectors $\mathbf{R}$ defined in Eq. (1.15). This more general type of crystals consists of basis atoms at positions $\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n$ for the case with n basis atoms. The positions of the atoms can then be defined as

$$\mathbf{R}_{\text{site}} = \mathbf{r}_u + \sum_{k=1}^d n_k \mathbf{a}_k, \quad u = 1, \dots, n \text{ and } n_k \in \mathbb{Z} \forall k = 1, \dots, d. \quad (1.16)$$

A two-dimensional ($d = 2$) Bravais lattice is shown in Fig. 1.9a), while a non-Bravais lattice is shown in Fig. 1.9b).

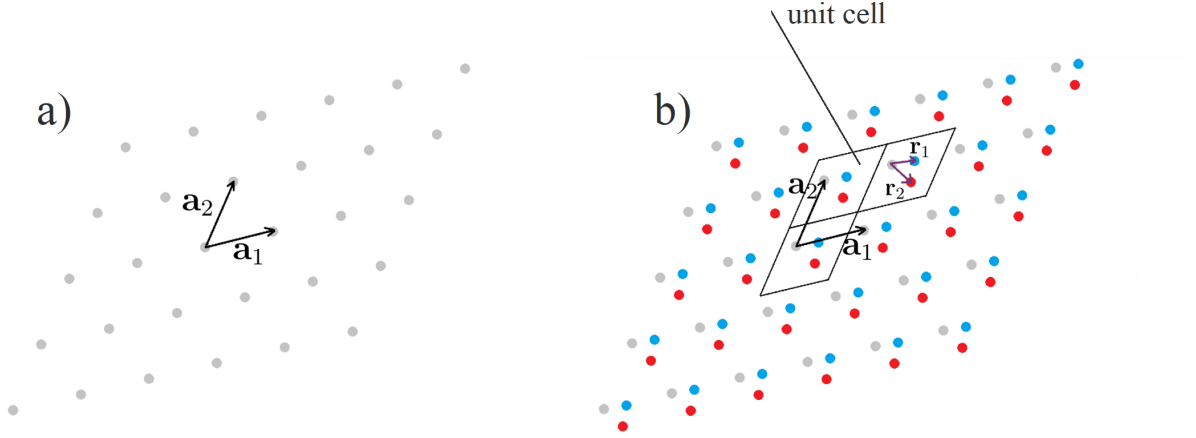


Figure 1.9: **a)** Some two-dimensional Bravais lattice **b)** A non-Bravais lattice with the same underlying primitive translations as the lattice in Panel **a)**.

Each site on a lattice can be a point in the domain of a function, such as the value of the spin at each lattice site. These functions can be represented as functions of space while their Fourier transform can be described as functions of wavevector. The space of wavevectors, also called “momentum space” is often preferred over real space when analyzing properties of crystals such as neutron scattering. For this reason, it is important to know the restriction on the possible wave vectors allowed for a lattice. For a finite-size parallelepiped lattice of the form $n_k = 1, \dots, L_k$ for $k = 1, 2, 3$ in Eq. (1.15), the set of wavevectors that respect periodic boundary conditions are

$$\mathbf{k} = \frac{m_1}{L_1} \mathbf{b}_1 + \frac{m_2}{L_2} \mathbf{b}_2 + \frac{m_3}{L_3} \mathbf{b}_3, \quad m_1, m_2, m_3 \in \mathbb{Z}. \quad (1.17)$$

This means that wavevectors in a material periodic boundary conditions are discretized for systems with a finite size, but in the limit of infinite systems the wavevectors can be continuous. Another property of wavevectors in a lattice is that there are infinitely many wavevector whose corresponding sinusoidal waves evaluate to the same function in the points of the lattice sites. This means that, when taking a Fourier transform of a function of the lattice points in space, a wavevector is not unique. For instance, given some special vector $\mathbf{G}$, two sinusoidal functions of the form $f_{\mathbf{k}}(\mathbf{R}) = e^{i\mathbf{k} \cdot \mathbf{R}}$ and $f_{\mathbf{k}+\mathbf{G}}(\mathbf{R}) = e^{i(\mathbf{k}+\mathbf{G}) \cdot \mathbf{R}}$ whose domain is restricted to the set of lattice points would be the same function if

$$e^{i(\mathbf{k}+\mathbf{G}) \cdot \mathbf{R}} = e^{i\mathbf{k} \cdot \mathbf{R}} \quad \forall \mathbf{R} \text{ satisfying Eq. (1.15)}. \quad (1.18)$$

We see which vector $\mathbf{G}$ would fulfill the condition in Eq. (1.18), which is when

$$\begin{aligned}\exp(i\mathbf{R} \cdot \mathbf{G}) &= 1 \\ \Rightarrow \mathbf{R} \cdot \mathbf{G} &= 2\pi n \text{ for some } n \in \mathbb{Z}.\end{aligned}\tag{1.19}$$

For all purposes in this thesis, lattices investigated in this thesis are three-dimensional ($d = 3$ in Eq. (1.15)-(1.16)). This definition of $d = 3$ is ideal for defining the reciprocal lattice: The cases $\mathbf{R} = \mathbf{a}_i$ for $i = 1, 2, 3$ can be used, along with $\mathbf{G} = \mathbf{b}_j$, to force

$$\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij}.\tag{1.20}$$

The vectors that would satisfy Eq. (1.20) are

$$\begin{aligned}\mathbf{b}_1 &= 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}, \\ \mathbf{b}_2 &= 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}, \\ \mathbf{b}_3 &= 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}.\end{aligned}\tag{1.21}$$

In the two-dimensional case, the cross-product formulae in Eq. (1.21) can still be used to get the reciprocal lattice vectors, by defining $\mathbf{a}_1, \mathbf{a}_2$ in the x - y plane, and then defining $\mathbf{a}_3$ to be in the $\hat{z}$ direction. One could then keep $\mathbf{b}_1$ and $\mathbf{b}_2$, while discarding $\mathbf{b}_3$. Back to the three-dimensional case, we can then define a general $\mathbf{G}$ vector that satisfies Eq. (1.18) as

$$\mathbf{G} = m_1\mathbf{b}_1 + m_2\mathbf{b}_2 + m_3\mathbf{b}_3.\tag{1.22}$$

Eq. (1.22) looks exactly like Eq. (1.15), except $\mathbf{G}$ is a vector in a lattice that consists of wavevectors, or a lattice in momentum space. This lattice is called the “reciprocal lattice”. Another thing to consider is that for a wavevector $\mathbf{k}$ propagating through the lattice, $\mathbf{k} + \mathbf{G}$ is equivalent to $\mathbf{k}$ for any reciprocal lattice vector $\mathbf{G}$. This redundancy in momentum space means that the Fourier transform of a function of the lattice should restrict $\mathbf{k}$ to a “Brillouin zone”. A Brillouin zone (BZ) is a set of wavevectors where no two wavevectors in the set are related to each other by a reciprocal lattice translation. With this restriction on the wavevectors of the lattice, combined with the restriction Eq. (1.17) for finite-sized systems, we have a set of valid wavevectors that can be used in the Fourier transform relations in a Bravais lattice:

$$\begin{aligned}\hat{f}(\mathbf{k}) &= \frac{1}{N_{\text{cells}}} \sum_{\mathbf{R}} f(\mathbf{R})e^{-i\mathbf{k} \cdot \mathbf{R}}, \\ f(\mathbf{R}) &= \sum_{\mathbf{k} \in \text{BZ}} \hat{f}(\mathbf{k})e^{i\mathbf{k} \cdot \mathbf{R}},\end{aligned}\tag{1.23}$$

where N_{cells} is the number of unit cells. For a non-Bravais lattice with n sublattice sites, the lattice functions in Eq.(1.23) depend on the sub lattice index:

$$\begin{aligned}\hat{f}_u(\mathbf{k}) &= \frac{1}{N_{\text{cells}}} \sum_{\mathbf{R}} f(\mathbf{R}) e^{-i\mathbf{k} \cdot (\mathbf{R} + \mathbf{r}_u)}, \\ f_u(\mathbf{R}) &= \sum_{\mathbf{k} \in \text{BZ}} \hat{f}(\mathbf{k}) e^{i\mathbf{k} \cdot (\mathbf{R} + \mathbf{r}_u)},\end{aligned}\tag{1.24}$$

for sublattice index $u = \{0, 1, \dots, n-1\}$. In this thesis, it is shown that some properties of a system, such as spin-spin correlations, are easier to analyze in momentum space.

1.2.2 Face-Centered-Cubic Lattice

The model for $\text{CuAlCr}_4\text{S}_8$ is a breathing pyrochlore, which not a Bravais lattice. However, the primitive translations of the breathing pyrochlore form an underlying Bravais lattice, called face-centered-cubic (FCC). The FCC lattice is a Bravais lattice where

$$\begin{aligned}\mathbf{a}_1 &= \frac{a}{2} (\hat{x} + \hat{y}), \\ \mathbf{a}_2 &= \frac{a}{2} (\hat{x} + \hat{z}), \\ \mathbf{a}_3 &= \frac{a}{2} (\hat{y} + \hat{z}),\end{aligned}\tag{1.25}$$

where a is the edge-length of the cube. The lattice is illustrated in Fig. 1.10.

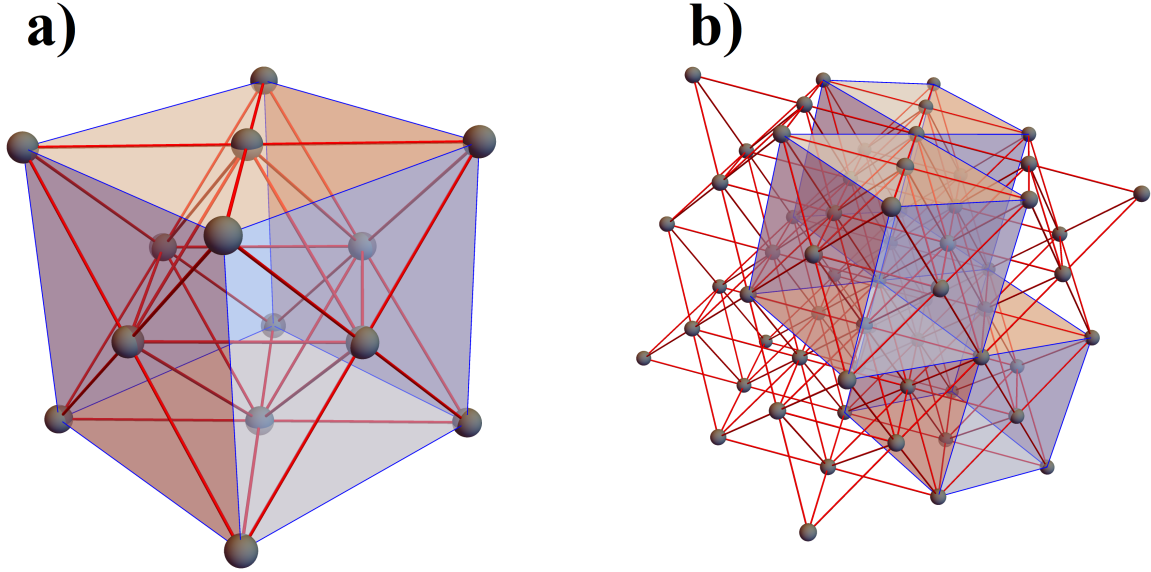


Figure 1.10: FCC lattice visualization **a)** A single cubic unit **b)** A larger portion of the lattice, with the same cubic units marked for reference. Notice that the lattice sites, marked with gray balls, are located at the corners of the cubes and at the centers of the faces of the cubic units.

1.2.3 Regular Pyrochlore

The pyrochlore lattice has the same lattice translation vectors as FCC, but unlike FCC, it is not Bravais. The pyrochlore lattice has a basis consisting of four sublattice sites with sublattice vectors

$$\begin{aligned}
 \mathbf{r}_0 &= \mathbf{0}, \\
 \mathbf{r}_1 &= \mathbf{a}_1/2, \\
 \mathbf{r}_2 &= \mathbf{a}_2/2, \\
 \mathbf{r}_3 &= \mathbf{a}_3/2.
 \end{aligned} \tag{1.26}$$

This geometry forms “up-facing” and “down-facing” tetrahedra, as shown in Fig. 1.11a), with lattice sites on the vertices of the corner-sharing tetrahedra. In the case of the regular pyrochlore, the up tetrahedra are reflections of the down tetrahedra; All tetrahedra are identical up to a reflection. This means that the pyrochlore has inversion symmetry.

1.2.4 Breathing Pyrochlore

Breathing pyrochlore emerge when tetrahedra in a pyrochlore lattice expand and contract [31]. In this case, the sublattice vectors are

$$\begin{aligned}\mathbf{r}_0 &= \mathbf{0}, \\ \mathbf{r}_1 &= \frac{\gamma}{\gamma+1}\mathbf{a}_1, \\ \mathbf{r}_2 &= \frac{\gamma}{\gamma+1}\mathbf{a}_2, \\ \mathbf{r}_3 &= \frac{\gamma}{\gamma+1}\mathbf{a}_3,\end{aligned}\tag{1.27}$$

where γ is the geometric breathing ratio. Unlike the regular pyrochlore, the up-facing tetrahedra are not mere reflections of the down tetrahedra. This assymetry could be due to the up-facing and down-facing tetrahedra having different sizes, as shown in Fig. 1.11b), or the tetrahedra could have other differing properties besides size, such different as nearest-neighbour exchange couplings between the spins on the sites.

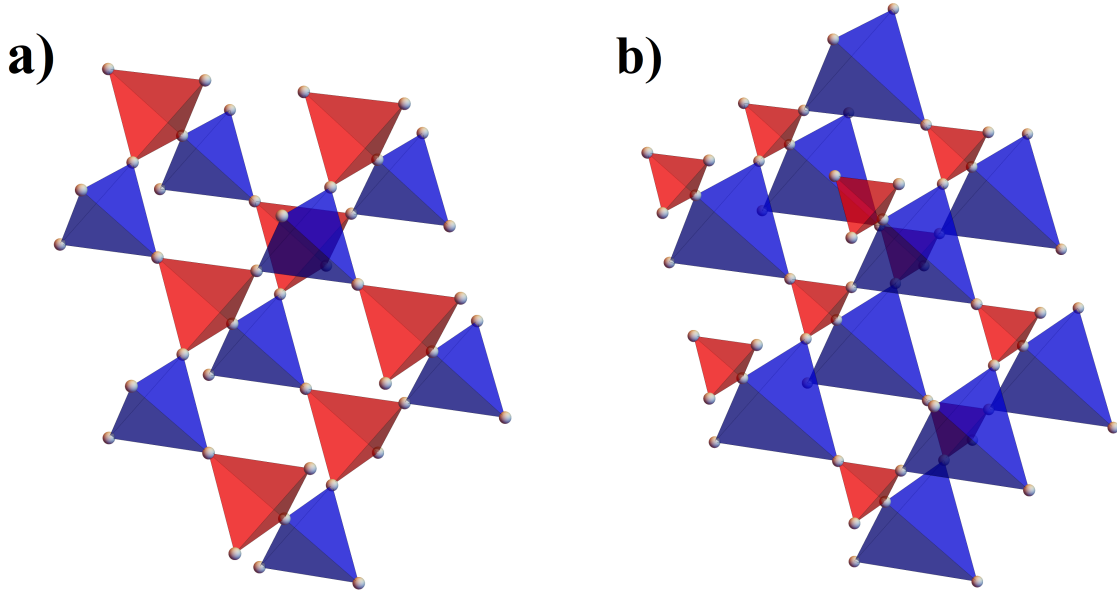


Figure 1.11: **a)** Regular pyrochlore lattice, with lattice sites at the corners of the tetrahedra. **b)** Breathing pyrochlore lattice, with alternating tetrahedra sizes. The breathing pyrochlore could also look like Panel **a)** as long as there is some other property that differentiates between the red and blue tetrahedra, such as having different nearest-neighbour exchange couplings.

1.3 Chromium Spinels

With the pyrochlore lattices defined, we now refer to real materials that have this lattice structure. The most common family of pyrochlores that have been explored have the chemical formula $(A^{3+})_2(B^{4+})_2(O^{2-})_7$, where A is typically a rare-earth ion and B is typically a transition metal. The A atoms and the B atoms are each arranged on their own pyrochlore lattices [32]. The chromium spinels are pyrochlores of a different type, $AA'Cr_4X_8$ where A is one of Li, Cu while A' is one of {Ga, In, Al}, and X is a chalcogen (one of O, S, Se) [33]. There is a group of chromium spinels, including $CuAlCr_4S_8$, that were first synthesized by H. L. Pinch *et. al* in 1970 [34]. The chromium spinels are topics of recent research, with expanding theoretical and experimental research [4, 35]. $CuAlCr_4S_8$ is a candidate for being a frustrated breathing pyrochlore [33], among other chromium spinels [4]. Chromium spinels have relatively small geometric breathing ratios $\gamma \sim 1.05 - 1.10$ (γ in

Eq. (1.27)) when compared with $\text{Ba}_3\text{Yb}_2\text{Zn}_5\text{O}_{11}$, which has a more pronounced asymmetry with a geometric breathing ratio of $\gamma \sim 2$ [36, 37]. From the experimental and theoretical information we have so far, the ordering mechanism for spins in $\text{CuAlCr}_4\text{S}_8$ is an ongoing area of research [33], and is the forefront topic of this thesis.

Model Hamiltonian

The Heisenberg spin Hamiltonian has the form

$$\mathcal{H} = \frac{1}{2} \sum_{ij} \mathcal{J}_{ij} \mathbf{S}_i \cdot \mathbf{S}_j, \quad (1.28)$$

where the $1/2$ factor is to eliminate double counting. This model is the Heisenberg model, where the interactions between spins depend on the scalar product of classical spins, which are normalized vectors in three dimensions. This is in contrast with the XY -model, which treated spins as unit vectors in a two-dimensional plane, or the Ising model, which restricted the spins to be one of the “up” or “down” states. This Heisenberg model is based on the exchange coupling that arises due to quantum mechanics [38, 39], which is explained in Section 1.4. Although the Heisenberg model arises from quantum phenomena, the spins are treated as classical vectors (i.e. having a definite state). A more accurate analysis would be to treat spins as quantum states. However, dealing with exact quantum spins comes with a computational complexity that modern computers cannot handle. In the Heisenberg model that is used for $\text{CuAlCr}_4\text{S}_8$, the interaction between a pair of spins depends on the *type* of neighbours. There is a nearest-neighbour-interaction for spins that share an edge on a small tetrahedron (J_{1a} coupling), an interaction for spins that share an edge on the large tetrahedron (J_{1b}), an interaction for spins that are the next nearest neighbours (J_2), and so on for further-apart neighbours. This means that $\text{CuAlCr}_4\text{S}_8$ is modeled by the following Hamiltonian

$$\mathcal{H} = \frac{1}{2} \sum_n J_n \sum_{\langle ij \rangle \in \mathcal{N}(n)} \mathbf{S}_i \cdot \mathbf{S}_j, \quad (1.29)$$

where $\langle ij \rangle \in \mathcal{N}(n)$ means “sites i and j are n^{th} -nearest-neighbours”, the neighbours’ index n follows the sequence (1a, 1b, 2, 3a, 3b, 4, 5, ...), with the displacement corresponding to each type of neighbour shown in Fig. 1.12.

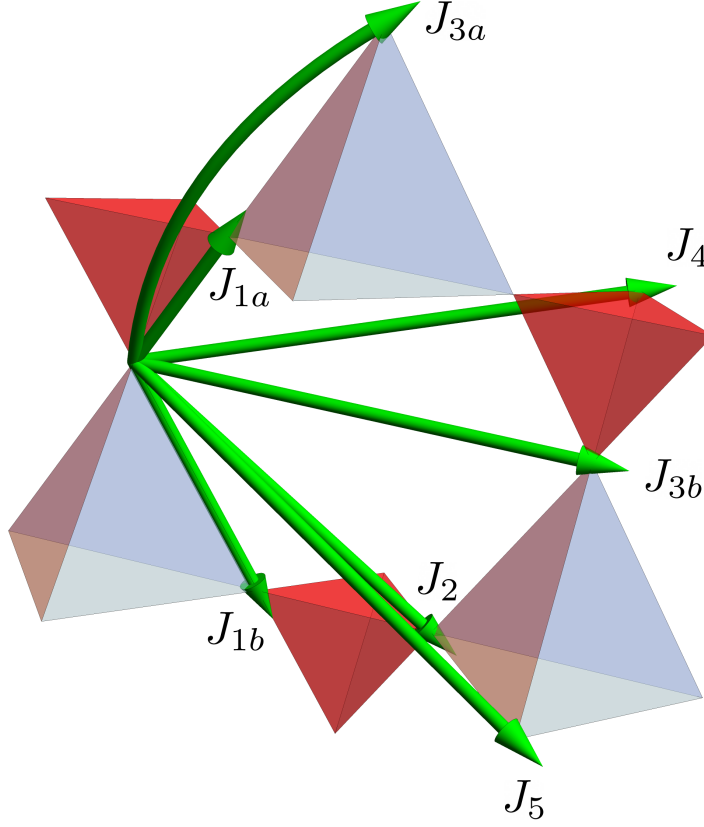


Figure 1.12: Subset of the tetrahedra that form a breathing pyrochlore, where the lattice sites are at the corners of the tetrahedra. Arrows show displacements between small-tetrahedron-edge nearest neighbours (exchange coupling J_{1a}), large-tetrahedron-edge nearest neighbours (exchange coupling J_{1b}), second-nearest neighbours (J_2), direct third-nearest neighbours (J_{3a}), indirect third-nearest neighbours (J_{3b}), fourth-nearest (J_4) and fifth-nearest (J_5) neighbours. Definition of neighbours is the same as the one used for the breathing pyrochlore in Ref. [1], with the labeling difference from there to here being $J \rightarrow J_{1a}$, $J' \rightarrow J_{1b}$. For explicit list of displacement vectors corresponding to each type of neighbour, refer to Appendix A.

Unique Properties

A magnetic crystal's spins are contributed by the spins of unpaired electrons. For the chromium spinels, the unpaired electrons in the magnetic Cr^{3+} ions are $3d$ -orbital electrons as opposed to the more commonly studied rare-earth pyrochlores whose unpaired electrons are from the $4f$ -orbitals. As a consequence, which is further explained in Section 1.4, the critical temperatures of chromium spinels' spin configurations are higher (~ 10 K) [33] when compared with rare-earth pyrochlores' critical temperatures (~ 1 K) [32, 37, 40]. The relatively high critical temperature, at around 20 K, makes $\text{CuAlCr}_4\text{S}_8$ experimentally viable for studying the ordering of the spins [33]. $\text{CuAlCr}_4\text{S}_8$ also has a property that makes it unique among the chromium spinels. When compared with the other chromium spinels in Table 1.1, one can see that $\text{CuAlCr}_4\text{S}_8$ is unique for having its strongest exchange coupling between third-nearest neighbours. The displacements between third-nearest-neighbour are the FCC primitive translations, which means that one could view $\text{CuAlCr}_4\text{S}_8$ four FCC lattices with perturbations. This special set coupling in $\text{CuAlCr}_4\text{S}_8$ gives an opportunity to test existing theoretical methods on a material whose types of Heisenberg exchange couplings have a unique nature.

Material	T (K)	J_{1a} (K)	J_{1b} (K)	J_2 (K)	J_{3a} (K)	J_{3b} (K)
$\text{LiInCr}_4\text{O}_8$	298	59.8(2)	22.0(2)	0.3(1)	1.9(1)	0.9(1)
$\text{LiGaCr}_4\text{O}_8$	298	66.2(3)	100.0(2)	0.7(1)	2.0(1)	1.3(1)
$\text{LiInCr}_4\text{S}_8$	298	-0.3(1)	-28.0(1)	0.7(1)	5.3(1)	2.4(1)
$\text{LiGaCr}_4\text{S}_8$	298	-7.7(1)	-12.2(1)	1.2(1)	6.1(1)	3.0(1)
$\text{CuInCr}_4\text{S}_8$	298	14.7(1)	-26.0(1)	1.1(1)	6.4(1)	4.5(1)
$\text{LiInCr}_4\text{Se}_8$	298	-25.4(2)	-31.0(1)	0.3(1)	4.8(1)	3.9(1)
$\text{LiInCr}_4\text{O}_8$	20	40.6(2)	40.8(2)	0.3(1)	2.0(1)	0.9(1)
$\text{LiInCr}_4\text{S}_8$	10	-10.8(1)	-9.5(1)	1.2(1)	6.2(1)	3.1(1)
$\text{CuAlCr}_4\text{S}_8$	12	-0.2(2)	-2.7(2)	0.1(1)	6.0(1)	3.5(1)

Table 1.1: Table of exchange couplings for various chromium spinels, obtained via a method called density-functional theory (DFT). The titular material, $\text{CuAlCr}_4\text{S}_8$, is at the bottom row, marked in red. All entries except for the bottom row are reported in Ref. [4], and the parameters for $\text{CuAlCr}_4\text{S}_8$ were obtained from our collaborators. The dominant third-nearest-neighbour couplings in $\text{CuAlCr}_4\text{S}_8$ are highlighted in blue. The T column is the temperature for which the exchange couplings are derived.

1.4 Mechanisms Behind Magnetism in Crystals

In the previous section, we discussed “what” is the model for $\text{CuAlCr}_4\text{S}_8$. While the Hamiltonian was listed in the previous section, there is a physical basis for how such an Hamiltonian arises in real materials. There are also other possible interactions in real systems that could modify the Hamiltonian, but there are arguments for why they can be neglected in $\text{CuAlCr}_4\text{S}_8$ as a reasonable first approximation.

1.4.1 Exchange Interactions

The subatomic particles involved in the bulk of inter-atomic interactions are electrons. Electrons are fermions, which means that if there is a joint wavefunction of multiple electrons, swapping a pair of electrons flips the sign of the wavefunction. This restriction on the wavefunctions, combined with existing Coulomb interaction between charged particles like electrons, results in particular types of interactions and effective Hamiltonians.

Isotropic Exchange

Depending on the orbitals of interacting electrons, exchange interactions can be ferromagnetic or antiferromagnetic. The derivation below is from Chapter 2 of *Lectures Notes on Electron Correlation and Magnetism* (Fazekas, 1999) [39].

Given the joint wavefunction of n fermions,

$$\psi((\mathbf{r}_1, \sigma_1), (\mathbf{r}_2, \sigma_2), \dots, (\mathbf{r}_n, \sigma_n)), \quad (1.30)$$

Where $\mathbf{r}_i$ is the position of electron i and σ_i is its spin. Let P_{ij} be the particle exchange operator that swaps electron i with electron j , then the joint wavefunction in Eq. (1.30) must satisfy

$$P_{ij}\psi = -\psi. \quad (1.31)$$

This restricts the type of many-electron wave functions that are possible. For example, consider the hydrogen molecule Hamiltonian

$$\begin{aligned}
\mathcal{H} = & H_{\text{atom}}(\mathbf{r}_1 - \mathbf{R}_a) + H_{\text{atom}}(\mathbf{r}_2 - \mathbf{R}_b) \\
& - \frac{e^2}{|\mathbf{r}_1 - \mathbf{R}_b|} - \frac{e^2}{|\mathbf{r}_2 - \mathbf{R}_a|} \\
& + \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \\
& + \frac{e^2}{|\mathbf{R}_a - \mathbf{R}_b|}.
\end{aligned} \tag{1.32}$$

where $\mathbf{R}_a, \mathbf{R}_b$ are the positions of the positively charged nuclei, $\mathbf{r}_1, \mathbf{r}_2$ are the positions of the electrons, $e = 1.6 \times 10^{-19}$ C is the elementary charge, and $H_{\text{atom}}(\mathbf{r})$ is the single hydrogen-atom hamiltonian for an electron and a nucleus separated by displacement $\mathbf{r}$. Let $\varphi_a(\mathbf{r}) = \varphi_{1s}(\mathbf{r} - \mathbf{R}_a)$ and $\varphi_b(\mathbf{r}) = \varphi_{1s}(\mathbf{r} - \mathbf{R}_b)$ be the eigenstates of single-atom Hamiltonian terms in Eq. (1.32), and define the real-space overlap integral

$$l := \int \varphi_a^*(\mathbf{r}) \varphi_b(\mathbf{r}) d\mathbf{r}. \tag{1.33}$$

Note that all the operators in $\mathcal{H}$ defined in Eq. (1.32) commute with spin operators, therefore the total spin S , and the z -component of the spin, S^z , are good quantum numbers. Thus, it can be assumed that the eigenstates of the two-atom Hamiltonian are linear combinations of S and S^z eigenstates. The four eigenstates are as follows:

$$|\psi_1\rangle = \frac{1}{\sqrt{2(1-l^2)}} \alpha(s_1) \alpha(s_2) [\varphi_a(\mathbf{r}_1) \varphi_b(\mathbf{r}_2) - \varphi_a(\mathbf{r}_2) \varphi_b(\mathbf{r}_1)], \tag{1.34}$$

$$|\psi_2\rangle = \frac{1}{2\sqrt{1-l^2}} [\varphi_a(\mathbf{r}_1) \varphi_b(\mathbf{r}_2) - \varphi_a(\mathbf{r}_2) \varphi_b(\mathbf{r}_1)] [\alpha(s_1) \beta(s_2) + \beta(s_1) \alpha(s_2)], \tag{1.35}$$

$$|\psi_3\rangle = \frac{1}{2\sqrt{(1-l^2)}} \beta(s_1) \beta(s_2) [\varphi_a(\mathbf{r}_1) \varphi_b(\mathbf{r}_2) - \varphi_a(\mathbf{r}_2) \varphi_b(\mathbf{r}_1)], \tag{1.36}$$

$$|\psi_4\rangle = \frac{1}{2\sqrt{1+l^2}} [\varphi_a(\mathbf{r}_1) \varphi_b(\mathbf{r}_2) + \varphi_a(\mathbf{r}_2) \varphi_b(\mathbf{r}_1)] [\alpha(s_1) \beta(s_2) - \beta(s_1) \alpha(s_2)], \tag{1.37}$$

where $\alpha(s)$ is the wavefunction at atom a for spin s , and $\beta(s)$ is the wavefunction at atom b for spin s . Let

$$\epsilon_{\text{at}} = \langle \psi_i | H_{\text{atomic}} | \psi_i \rangle, \quad (1.38)$$

which is the same single-atom energy for the eigenstates $|\psi_1\rangle, |\psi_2\rangle, |\psi_3\rangle, |\psi_4\rangle$. When evaluating the expectation energies of $|\psi_1\rangle, |\psi_2\rangle, |\psi_3\rangle$, we get a triplet with energy

$$\epsilon_{\text{t}} = \langle \psi_i | \mathcal{H} | \psi_i \rangle = 2\epsilon_{\text{at}} + \frac{C_{ab} - I_{ab}}{1 - l^2}, \quad (1.39)$$

where C_{ab} is the term from the Coulomb interaction between the charges, weighted by their probability distribution in space, given by

$$\begin{aligned} C_{ab} = & \int d\mathbf{r}_1 \int d\mathbf{r}_2 |\varphi_a(\mathbf{r}_1)|^2 \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} |\varphi_b(\mathbf{r}_2)|^2 - \int d\mathbf{r}_1 \frac{e^2}{|\mathbf{r}_1 - \mathbf{R}_b|} |\varphi_a(\mathbf{r}_1)|^2 \\ & - \int d\mathbf{r}_2 \frac{e^2}{|\mathbf{r}_2 - \mathbf{R}_a|} |\varphi_b(\mathbf{r}_2)|^2. \end{aligned} \quad (1.40)$$

I_{ab} is the exchange term, which involves the overlap between different atoms' wavefunctions

$$\begin{aligned} I_{ab} = & \int d\mathbf{r}_1 \int d\mathbf{r}_2 \varphi_a^*(\mathbf{r}_1) \varphi_b(\mathbf{r}_1) \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \varphi_b^*(\mathbf{r}_2) \varphi_a(\mathbf{r}_2) \\ & - l \int d\mathbf{r}_1 \frac{e^2}{|\mathbf{r}_1 - \mathbf{R}_b|} \varphi_a^*(\mathbf{r}_1) \varphi_b(\mathbf{r}_1) - l \int d\mathbf{r}_2 \frac{e^2}{|\mathbf{r}_2 - \mathbf{R}_a|} \varphi_b^*(\mathbf{r}_2) \varphi_a(\mathbf{r}_2). \end{aligned} \quad (1.41)$$

Meanwhile, the singlet energy is

$$\epsilon_s = \langle \psi_4 | \mathcal{H} | \psi_4 \rangle = 2\epsilon_{\text{at}} + \frac{C_{ab} + I_{ab}}{1 + l^2}, \quad (1.42)$$

which gives an energy difference of

$$\epsilon_{\text{tr}} - \epsilon_{\text{s}} = 2 \frac{l^2 C_{ab} - I_{ab}}{1 - l^4}. \quad (1.43)$$

Note that the eigenstates can be represented as the triplet states

$$|\psi_1\rangle := |1, 1\rangle, \quad |\psi_2\rangle := |1, 0\rangle, \quad |\psi_3\rangle := |1, -1\rangle, \quad (1.44)$$

and the singlet is

$$|\psi_4\rangle = |0, 0\rangle, \quad (1.45)$$

where $|s, m\rangle$ means “|total spin- s , total s_z ⟩”, the spatial dependence of each eigenstate is shown in Eqs. (1.34)-(1.37). Noting that

$$(\mathbf{S}_1 + \mathbf{S}_2)^2 |\psi_i\rangle = \begin{cases} 2|\psi_i\rangle & \text{for a triplet (if } i = 1, 2, 3) \\ 0|\psi_i\rangle & \text{for a singlet (if } i = 4) \end{cases}, \quad (1.46)$$

to get that

$$2\mathbf{S}_1 \cdot \mathbf{S}_2 + \frac{1}{2} = (\mathbf{S}_1 + \mathbf{S}_2)^2 - 1 = \begin{cases} 1 & \text{for a triplet} \\ -1 & \text{for a singlet} \end{cases}. \quad (1.47)$$

This means that the Hamiltonian can be defined as

$$\begin{aligned} \mathcal{H} &\rightarrow \frac{\epsilon_s + \epsilon_{\text{tr}}}{2} - \frac{\epsilon_s - \epsilon_{\text{tr}}}{2} (2\mathbf{S}_1 \cdot \mathbf{S}_2 + \frac{1}{2}) \\ &= \text{constant} + J_{12} \mathbf{S}_1 \cdot \mathbf{S}_2, \end{aligned} \quad (1.48)$$

where

$$J_{12} = 2 \frac{l^2 C_{ab} - I_{ab}}{1 - l^4}. \quad (1.49)$$

For sufficiently large overlap integral l , $l^2 C_{ab} > I_{ab}$, giving antiferromagnetic exchange, while in the case of orthogonal orbitals that have 0 overlap, $J_{12} = -I_{ab} < 0$ and the exchange is ferromagnetic. If the absolute energy does not matter and only the differences in energy levels matter, then the constant energy terms in the Hamiltonian can be ignored to write the Hamiltonian as

$$\mathcal{H}_{\text{eff}} = J_{12} \mathbf{S}_1 \cdot \mathbf{S}_2, \quad (1.50)$$

which is the two-site Heisenberg model. This gives us insight at how the hydrogen molecule, one of the simplest compounds, can have exchange interaction between its electrons. In more complicated system, the exchange interaction still plays a role. The example shown is for direct exchange between two electrons. Exchange interactions can be more complicated and involve more particles, with information available in Refs. [39, 41]. For more complicated atoms, finding the exact exchange couplings from first principles without utilizing any experimental measurements is extremely challenging if at all possible. To counter this complication, one can extract the couplings based on experimental measurements mixed with fitting parameters to the experimental data [42].

Anisotropic Interactions

Spin-orbit coupling occurs when the orbital of an electron generates a magnetic moment that interacts with the electron's spin. Spin-orbit coupling can be incorporated into a Hamiltonian by including a term $\lambda(\mathbf{S} \cdot \mathbf{L})$, where λ is the spin-orbit coupling intensity. Spin-orbit coupling generates anisotropy in the spin interactions, since the spin operator no longer commutes with real-space operators, due to the $\mathbf{L}$ operator depending on existing electric field in the crystal. When combined with exchange, spin-orbit couplings gives rise to anisotropic interactions in the spins, given by

$$\mathcal{H}_{\text{aniso}} = \mathbf{S} \cdot \mathbf{g} \cdot \mathbf{h} - \lambda^2 \mathbf{S} \cdot \mathbf{\Lambda} \cdot \mathbf{S} - \mu_B \mathbf{h} \cdot \mathbf{\Lambda} \cdot \mathbf{h}, \quad (1.51)$$

where λ is the spin-orbit coupling strength, $\mathbf{\Lambda}$ is a tensor depending on the geometry and orientation of the electron orbitals, $\mathbf{g}$ is a tensor satisfying $g_{ij} = 2(\delta_{ij} - \lambda \Lambda_{ij})$, and μ_B is the Bohr magneton, which has units of magnetic moment. The anisotropy in the spins gives rise to interactions such as Dzyaloshinskii-Moriya [43] among others [39]. For more information on anisotropic spin interactions, refer to Chapter 3 of *Lecture Notes on Electron Correlation and Magnetism* by Fazekas (1999) [39]. Since the unpaired electrons in Cr^{3+} ions are $3d$, which are the ion's outermost electrons, these electrons are highly influenced by the crystal field, which in spinel crystals splits the five $3d$ orbitals into a ground triplet (t_{2g}) and an excited doublet (e_g). The energy gap between the triplet and the doublet is $\sim 10^4$ K in chromium spinels, meaning that only the three t_{2g} orbitals are accessible at the temperatures of interest [44]. This means that the three $3d$ electrons in Cr^{3+} restricted to the three orbitals, and since Hund's second law still holds in spinels, each of the three orbitals is singly occupied. The single-occupation of each of the t_{2g} orbitals leads to a total orbital angular momentum $L = 0$ [39], meaning that spin-orbit coupling is negligible for Cr^{3+} ions in spinels. Thus, spin-orbit coupling and the anisotropic exchange that would result from it can be neglected for $\text{CuAlCr}_4\text{S}_8$.

1.4.2 Effect of Electronic Structure

In an atom, magnetic moments come from unpaired electrons [39]. Due to the Pauli exclusion principle, each electron orbital may contain up to two electrons, with opposite spins. This means that the magnetic moment of spins that are paired in the same orbital is effectively canceled out. Magnetic atoms have unpaired electrons, so that the atom's cumulative spin is nonzero.

Hund's Rules in Isolated Atoms

Hund's three rules describe the occupancy of electron orbitals in an isolated atom's ground state. The rules are as follows: the electrons fill the available states that result in the

1. largest value of total spin S
2. largest value of orbital angular momentum L that is permitted by the first rule (Hund's second rule)
3. total angular momentum being $J = |L - S|$ for less-than-half-filled shells and $J = |L + S|$ for more-than-half-filled shells (Hund's third rule)

Hund's rules may not necessarily hold when the atoms are in an external field, or coupled with other atoms in a compound.

Hund's Rules in interacting atoms

While rare-earth metals' $4f$ electrons are shielded by the outer $5s$ and $5p$ electrons, transition metals' $3d$ electrons are the outer electrons and are more strongly influenced by the electric fields of other atoms (crystal field), which causes Hund's third rule to become invalidated, and alters the atoms' total angular momentum J [39]. Still, Hund's first two rules generally hold in either case. For rare-earth ($4f$) electrons, the energy scales are

$$\text{exchange} > \text{spin-orbit coupling} > \text{crystal field}.$$

Meanwhile, for transition-metal ($3d$) electrons, the energy scales are usually but not always

$$\text{exchange} > \text{crystal field} > \text{spin-orbit coupling}.$$

When crystal fields dominate over spin-orbit coupling, as in the case of $3d$ electrons, the spin S and the orbit angular momentum L are good quantum numbers whose values can be determined by Hund's first and second rules. Meanwhile, J is not a good quantum number when the crystal field dominates over the spin-orbit coupling. The magnetic ion in $\text{CuAlCr}_4\text{S}_8$, Cr^{3+} , which has electron configuration $3d^3$, can be viewed as having a total angular momentum equal to the total spin ($J = S$) as a better approximation than Hund's third rule ($J = |L + S|$ or $J = |L - S|$). Thus, Cr^{3+} can be viewed as having a total angular momentum $J = 3/2$ since there are three electrons with spin-1/2 each [45].

1.4.3 Dipolar Interactions

The dipole energy exists due to pairwise interactions between magnetic moments,

$$\mathcal{H}_{\text{dip}} = \sum_{i \neq j} \frac{1}{r_{ij}^3} [\boldsymbol{\mu}_i \cdot \boldsymbol{\mu}_j - 3(\boldsymbol{\mu}_i \cdot \hat{\mathbf{r}}_{ij})(\boldsymbol{\mu}_j \cdot \hat{\mathbf{r}}_{ij})], \quad (1.52)$$

where $\mathbf{r}_{ij} = r_{ij}\hat{\mathbf{r}}_{ij}$ is the displacement between site i and site j , and $\boldsymbol{\mu}_i$ is the magnetic moment at site i , which is proportional to the spin at site i [31, 46, 47]. The goal is to show that dipolar interactions are negligible for $\text{CuAlCr}_4\text{S}_8$. One could express the dipolar Hamiltonian as

$$\mathcal{H}_{\text{dip}} = \sum_{ij} \sum_{\nu\mu} D_{ij}^{\nu\mu} s_i^\nu s_j^\mu, \quad (1.53)$$

where s_i^ν is the ν -component of the spin at site i . One could approximate the dipolar coupling coefficients as

$$D_{ij}^{\nu\mu} \leq \frac{\mu_0}{2\pi} \frac{g^2 \mu^2}{r_{ij}^3} \quad (1.54)$$

where μ is the dipole moment of a spin, $g \approx 2$ is a factor that characterises electrons, and μ_0 is the Bohr magneton [46]. $g\mu \approx 10.6$ for Dysprosium (Dy) while $g\mu \approx 3.7$ for Chromium (Cr) [45]. $\text{Dy}_2\text{Ti}_2\text{O}_7$ is a pyrochlore with a lattice constant of ≈ 10 Å [48], which is about the same as the lattice constant for $\text{CuAlCr}_4\text{S}_8$. This means that one expects dipole interactions at the nearest neighbor for $\text{CuAlCr}_4\text{S}_8$ to be $\frac{(g\mu_{\text{Dy}})^2}{(g\mu_{\text{Cr}})^2} \approx 10$ times weaker than $\text{Dy}_2\text{Ti}_2\text{O}_7$'s 2.35 K, which is at around ~ 0.2 K, much weaker than most of the given exchange couplings in $\text{CuAlCr}_4\text{S}_8$. The dipolar couplings decrease in space as $1/r^3$. which means that the dipolar coupling between fifth-nearest-neighbour couplings is about 10 times weaker than that of first nearest neighbours, which are a little closer than half of the fifth-NN's distance. Therefore, dipolar interactions can be neglected from the model for $\text{CuAlCr}_4\text{S}_8$. A remaining concern, however, is the range of dipolar interaction, which decay in distance as $1/r^3$ and thus have infinite range. It has been shown that for $\text{Dy}_2\text{Ti}_2\text{O}_7$, the correction to the Hamiltonian from dipolar interactions is within the same order of magnitude of the upper bound in Eq.(1.53), even when including dipolar

interactions up to distances as long as 100th-nearest-neighbours [49]. Since Dy₂Ti₂O₇ is a pyrochlore lattice with the same lattice dimensions as CuAlCr₄S₈'s within 2% difference, then similar displacement-dependent long-range dipolar contributions are expected according to Eq. (1.52). Therefore, the effect of dipolar interactions, which is negligible for nearest-neighbours in CuAlCr₄S₈, can also be assumed to be negligible for long-range dipolar interactions.

1.4.4 Biquadratic Interactions

We have ruled out the need to include anisotropic exchange and dipolar interactions in CuAlCr₄S₈. This leaves us with the isotropic exchange Hamiltonian, called the Heisenberg model,

$$\mathcal{H} = \sum_{ij} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j, \quad (1.55)$$

where J_{ij} are the exchange couplings between the spin $\mathbf{S}_i$ at site i and the spin $\mathbf{S}_j$ at site j . While it is convenient to assume that the positions of the spins in the crystal are held firmly in place, this is not guaranteed in real systems. In some crystals, there are non-negligible lattice deformations such as the Jahn-Teller effect, which complicate the spin-spin interactions [39]. This flexibility in the sites' positions leads to corrections in the Hamiltonian, including corrections that are biquadratic in the spins. We derive the energy correction that follow from the sites' displacements. The energy between two displaced spins can be expressed to linear order in displacement as

$$E_{ij} = [J_{ij} + \nabla_{\delta \mathbf{r}} J_{ij} \cdot \delta \mathbf{r}_{ij}] (\mathbf{S}_i \cdot \mathbf{S}_j), \quad (1.56)$$

where J_{ij} is the exchange coupling between spins $\mathbf{S}_i$ and $\mathbf{S}_j$, and the distance between the sites is $\mathbf{r}_{ij} = \mathbf{r}_0 + \delta \mathbf{r}_{ij}$ for some reference distance r_0 [50, 51]. In a many-body system, the energy of displacing spin sites can be expressed as

$$E = E_0 + \sum_{a,i,j} \frac{\partial J_{ij}}{\partial x_a} (\mathbf{S}_i \cdot \mathbf{S}_j) x_a + \sum_{a,b} \frac{k_{ab}}{2} x_a x_b, \quad (1.57)$$

where E_0 is the energy when the spins are fixed. a, b are indices of displacements of all lattice sites along each Cartesian component (if there are N_s sites, and 3 Cartesian components, then $a, b = 1, \dots, 3N_s$ is a possible enumeration). x_b is a component of a

displacement of a lattice site that is enumerated by index b , and k_{ab} are elastic coefficients depending on how easily the corresponding lattice sites can be stretched or compressed along certain Cartesian components. Define the following tensors, $\mathbf{T}$, $\partial\mathbf{J}/\partial\mathbf{x}$, and $\mathbf{x}$, where

$$\begin{aligned}\mathbf{T}_{ij} &= \mathbf{S}_i \cdot \mathbf{S}_j, \\ \left(\frac{\partial\mathbf{J}}{\partial\mathbf{x}}\right)_{ij,a} &= \frac{\partial J_{ij}}{\partial x_a}, \\ \mathbf{x}_a &= x_a,\end{aligned}\tag{1.58}$$

then the energy correction can be written in tensor form as

$$E - E_0 := \Delta E = \mathbf{T}^\dagger \frac{\partial\mathbf{J}}{\partial\mathbf{x}} \mathbf{x} + \frac{1}{2} \mathbf{x}^\dagger \mathbf{K} \mathbf{x}.\tag{1.59}$$

Consider a unitary transformation $\mathbf{U}$ such that $\mathbf{U}\mathbf{K}\mathbf{U}^\dagger$ is diagonal. Let

$$\mathbf{y} = \mathbf{U}\mathbf{x}, \Rightarrow \mathbf{x} = \mathbf{U}^\dagger \mathbf{y}.\tag{1.60}$$

This can be written out as

$$\begin{aligned}y_\alpha &= \sum_a U_{\alpha a} x_a, \\ x_a &= \sum_\alpha (U^\dagger)_{a\alpha} y_\alpha = \sum_\alpha y_\alpha U_{\alpha a}.\end{aligned}\tag{1.61}$$

By the chain rule

$$\begin{aligned}\frac{\partial J_{ij}}{\partial x_a} &= \sum_\alpha \frac{\partial J_{ij}}{\partial y_\alpha} \frac{y_\alpha}{\partial x_a} = \sum_\alpha \frac{\partial J_{ij}}{\partial y_\alpha} U_{\alpha a} = \left(\frac{\partial\mathbf{J}}{\partial\mathbf{y}} \mathbf{U}\right)_a, \\ &\Rightarrow \frac{\partial\mathbf{J}}{\partial\mathbf{x}} = \frac{\partial\mathbf{J}}{\partial\mathbf{y}} \mathbf{U}.\end{aligned}\tag{1.62}$$

Using this along with $\mathbf{U}\mathbf{U}^\dagger = \mathbb{I}$ in Eq. (1.59):

$$\begin{aligned}\Delta E &= \mathbf{T}^\dagger \frac{\partial\mathbf{J}}{\partial\mathbf{y}} \mathbf{U}\mathbf{U}^\dagger \mathbf{U}\mathbf{x} + \frac{1}{2} \mathbf{x}^\dagger \mathbf{U}^\dagger \mathbf{U}\mathbf{K}\mathbf{U}^\dagger \mathbf{U}\mathbf{x} \\ &= \mathbf{T}^\dagger \frac{\partial\mathbf{J}}{\partial\mathbf{y}} \mathbf{y} + \frac{1}{2} \mathbf{y}^\dagger \underbrace{\mathbf{U}\mathbf{K}\mathbf{U}^\dagger}_{\text{diagonal}} \mathbf{y}.\end{aligned}\tag{1.63}$$

Letting $(\mathbf{U}\mathbf{K}\mathbf{U}^\dagger)_{\alpha\beta} = \kappa_\alpha \delta_{\alpha\beta}$ since $\mathbf{U}$ diagonalizes $\mathbf{K}$, and expressing (1.59) in summation form gives

$$\Delta E = \sum_{\alpha} \left[\sum_{i,j} (\mathbf{S}_i \cdot \mathbf{S}_j) \frac{\partial J_{ij}}{\partial y_{\alpha}} y_{\alpha} + \frac{1}{2} \kappa_{\alpha} y_{\alpha}^2 \right]. \quad (1.64)$$

The goal is to minimize ΔE to see what happens in the low-temperature regime. Finding the minimum in the energy correction can be done by differentiating Eq. (1.64)

$$\frac{\partial E}{\partial y_{\alpha}} = \sum_{i,j} (\mathbf{S}_i \cdot \mathbf{S}_j) \frac{\partial J_{ij}}{\partial y_{\alpha}} + \left[\sum_{i,j} (\mathbf{S}_i \cdot \mathbf{S}_j) \frac{\partial^2 J_{ij}}{\partial y_{\alpha}^2} + \kappa_{\alpha} \right] y_{\alpha}, \quad (1.65)$$

and solving for $\partial E / \partial y_{\alpha} = 0$, which gives

$$y_{\alpha} = - \frac{\sum_{i,j} (\mathbf{S}_i \cdot \mathbf{S}_j) \frac{\partial J_{ij}}{\partial y_{\alpha}}}{\sum_{i,j} (\mathbf{S}_i \cdot \mathbf{S}_j) \frac{\partial^2 J_{ij}}{\partial y_{\alpha}^2} + \kappa_{\alpha}}. \quad (1.66)$$

If that the lattice is firm enough to only allow slight deformations, one can assume $\kappa_{\alpha} \gg \sum_{i,j} (\mathbf{S}_i \cdot \mathbf{S}_j) \frac{\partial^2 J_{ij}}{\partial y_{\alpha}^2}$, which simplifies Eq. (1.66) into

$$y_{\alpha} = - \frac{1}{\kappa_{\alpha}} \sum_{i,j} (\mathbf{S}_i \cdot \mathbf{S}_j) \frac{\partial J_{ij}}{\partial y_{\alpha}}. \quad (1.67)$$

Plugging Eq. (1.67) back into the energy correction in Eq. (1.64) gives

$$\Delta E = - \frac{1}{2} \sum_{\alpha} \frac{1}{\kappa_{\alpha}} \left[\sum_{i,j} (\mathbf{S}_i \cdot \mathbf{S}_j) \frac{\partial J_{ij}}{\partial y_{\alpha}} \right]^2. \quad (1.68)$$

By defining the four-site coefficient

$$C_{ijkl} = \sum_{\alpha} \frac{1}{\kappa_{\alpha}} \frac{\partial J_{ij}}{\partial y_{\alpha}} \frac{\partial J_{kl}}{\partial y_{\alpha}}, \quad (1.69)$$

Eq. (1.68) can be written as

$$\Delta E = - \frac{1}{2} \sum_{i,j,k,l} C_{ijkl} (\mathbf{S}_i \cdot \mathbf{S}_j) (\mathbf{S}_k \cdot \mathbf{S}_l), \quad (1.70)$$

where i, j, k, l are sites with spins $\mathbf{S}_i, \mathbf{S}_j, \mathbf{S}_k, \mathbf{S}_l$, respectively. If biquadratic interactions are non-negligible, this interaction would complicate many of the semi-analytical methods that are used to analyze the system, which are only suitable when the Hamiltonian has spin dependencies only up to quadratic order. Recalling that the reason for biquadratic interaction is displacement of the lattice sites, one could look at the structure of the lattice and check if there is a structural change at low temperatures, which would suggest that biquadratic interactions are significant, as seen in the $\text{LiGaCr}_4\text{O}_8$ chromium spinel [52]. There are still questions on whether biquadratic interactions are significant in $\text{CuAlCr}_4\text{S}_8$, but so far no significant distortions in the lattice structure has been observed by our collaborating experimentalists for $\text{CuAlCr}_4\text{S}_8$ above 10 K

1.5 Motivation Behind $\text{CuAlCr}_4\text{S}_8$

We provided the basis for magnetic crystals, how their spins interact, and how this all applies to $\text{CuAlCr}_4\text{S}_8$. We now refer to why frustrated magnetic systems are worthy of research, and why the material $\text{CuAlCr}_4\text{S}_8$, a frustrated breathing pyrochlore, is worthy of being studied.

Frustrated systems are candidates for exotic phenomena such as superconductivity [53–55], spin glasses [18, 56], spin liquids [57, 58], and spin ices. Spin ices and spin liquids have generated fruitful research due to their unique emergent electromagnetic theory [57, 59].

Within frustrated systems, there are pyrochlores. Pyrochlores are worth studying since their geometry allows for physical manifestations of frustrated magnetism, and there is a variety of pyrochlores that can be synthesized for experiments and modeled for theoretical research. Breathing pyrochlores add more unique possibilities, due to the breaking of inversion symmetry that exists in regular pyrochlores. The breathing pyrochlores have been a fertile ground for many unique phenomena. An example of a potential unique phenomenon in breathing pyrochlores is the emergence of rank-2 $\text{U}(1)$ spin liquids, where the emergent electromagnetic fields are tensors rather than the vectors in conventional rank-1 electromagnetism [60]. Breathing pyrochlores are also candidates for third-order topological insulators [61]. Breathing pyrochlores could also allow quantum spin liquids to have a much broader regime than regular pyrochlores, due to the structure of the breathing pyrochlore [57].

Within breathing pyrochlores, chromium spinels have relatively strong exchange interactions between their magnetic ions. The strength of these exchange couplings leads to critical temperatures at $O(10^1)$ K, which is relatively high and accessible to experiments

when compared to rare-earth pyrochlores, whose critical temperatures are typically $O(1)$ K [4]. Besides the favourable temperature scales of phase transitions, chromium spinels are candidates for several unique phenomena. For example, $\text{LiGa}_{0.95}\text{In}_{0.05}\text{Cr}_4\text{O}_8$ is a candidate for classical spin nematic transition [62], while there is cluster frustration [63] and negative thermal expansion predicted by the model for $\text{LiGaCr}_4\text{S}_8$ [64]. Existing chromium spinels may also host Weyl magnons, the spin system analogues of Weyl fermions, that can be manipulated by magnetic fields [65]. More unique properties for the breathing pyrochlores have been brought up in Refs. [66–74].

Within the chromium spinels, $\text{CuAlCr}_4\text{S}_8$ is special for its exchange coupling’s dependence on the distance between interacting neighbours. As can be seen in Table 1.1, $\text{CuAlCr}_4\text{S}_8$ has dominant 3rd-nearest-neighbour couplings (J_{3a} and J_{3b}) when compared with couplings between closer neighbours (J_{1a} , J_{1b} and J_2). This is in contrast with other explored chromium spinels that have strongest 1st-NN couplings and weaker 3rd-NN couplings. Moreover, $\text{CuAlCr}_4\text{S}_8$ has new experimental data [33], and theoretical analysis is important as a complementary information to the experimental data. It is possible to have experimental data that is missing information on its own, but theoretical models could give rise to predictions which, if consistent with the experimental data, could dramatically narrow down the possibilities for the model without needing further experiments. While this hope is often harder to realize in practice, it is possible to use theory alongside experiment rule out possible behaviours in the material. This means that supplementing existing experimental data on $\text{CuAlCr}_4\text{S}_8$ with theoretical predictions would be a chance to test the viability of said theoretical methods.

1.6 Thesis Overview

The research process started after the experimental results for $\text{CuAlCr}_4\text{S}_8$ were made available from Ref. [33]. This prompted our collaborators to model $\text{CuAlCr}_4\text{S}_8$ as a Heisenberg-model breathing pyrochlore, with exchange couplings going up to 3rd NN. The exchange couplings were obtained via DFT calculations. With the theoretical exchange couplings provided, MFT, large- N and classical Monte Carlo (CMC) simulations were used to predict the neutron-scattering structure factor of $\text{CuAlCr}_4\text{S}_8$, along with specific heat and susceptibility. At that point, our collaborators calculated the structure factor of the model using quantum methods. Later, more experimental data was made available by the authors of Ref. [33], specifically, neutron scattering off $\text{CuAlCr}_4\text{S}_8$ powder. The experimental data suggested that there are magnetic Bragg peaks at different wavevectors from the ones predicted by theoretical methods that implement the up-to-3rd-NN model. As an attempt to

provide a more accurate model, our collaborators provided an updated model using DFT to include exchange couplings up to 5th-nearest-neighbours. Since the updated model was provided, the classical methods used in this thesis were redone on the updated exchange coupling. The results from classical methods using both the initial up-to-3rd NN and the newer up-to-5th NN Heisenberg model are shown in this thesis.

In Chapter 2, we discuss the basis for describing spin-spin correlations, and the semi-analytical methods that are used to analyze the Heisenberg model on the breathing pyrochlore. The semi-analytical methods are MFT and large- N , and the numerical method is CMC simulations. Chapter 3 contains results from the semi-analytical methods and comparisons with our collaborators' other methods where applicable. Chapter 4 contains results from numerical CMC simulations, which are also compared with collaborators' work. In Chapter 5, we discuss the significance of the results, conclude the key points from the research so far, and provide ideas for the next steps.

Chapter 2

Methods

2.1 System Measurements

2.1.1 Neutron Scattering

Particles with momentum $\mathbf{p}$ have an associated de Broglie wavevector $\mathbf{k}$ satisfying

$$\mathbf{p} = \hbar\mathbf{k}, \tag{2.1}$$

where $\hbar = 1.054571817 \times 10^{-34} \text{J}\cdot\text{s}$ is the reduced Planck constant, here acting as a conversion factor between wavevector and momentum [75]. The relationship between wavevectors and momentum is useful for determining structural properties of lattices. This is so because translational symmetries in the lattice correspond to wavevectors, which can interact with incident particles via momentum transfer. Indeed, one can learn about the periodic nature of a crystal by firing particles at the crystal and investigating the momentum of the scattered particles. To study the periodicity of spin orientations in the lattice, it is beneficial to use scattering particles that mainly interact with the lattice by spin-spin interactions. The neutron is a prime candidate, since it has a spin but no charge, which means that the scattering of neutrons in a sample can be attributed to spin-spin correlations rather than electrostatic interactions. This property makes neutron scattering an idea to probe the magnetic interactions or correlations in materials. For the readers interested in the technical properties of neutron scattering, please refer to [75, 76].

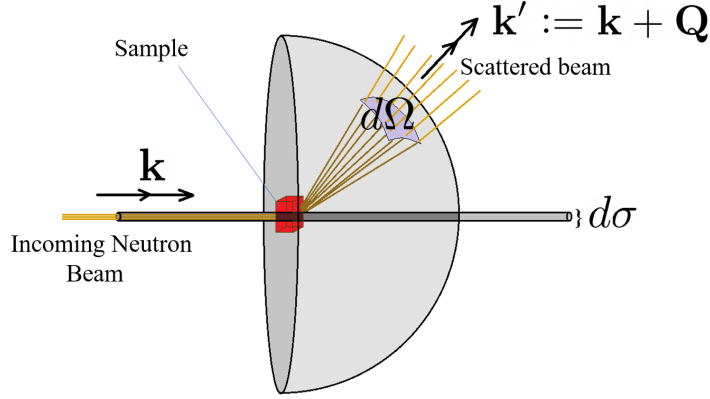


Figure 2.1: Schematic of neutron scattering. A beam of neutrons with wavevector $\mathbf{k}$ is fired at a sample. The neutrons interact with the particles in the lattice via magnetic interactions and get scattered. For a given scattered beam with out-going wavevector $\mathbf{k}'$, the solid angle spanned by the beam depends on several variables, including the magnetic correlations of spins in the sample.

For a neutron with initial momentum $\mathbf{p}$ that scatters off a material with final momentum $\mathbf{p}'$, conservation of momentum means that the lattice receives a momentum $\Delta\mathbf{p}$ from the neutron such that

$$\Delta\mathbf{p} = \mathbf{p} - \mathbf{p}'. \quad (2.2)$$

Expressing momentum transfer from a scattered neutron in terms of wavevectors using Eq. (2.1) gives

$$\mathbf{Q} = \mathbf{k} - \mathbf{k}', \quad (2.3)$$

where $\mathbf{k} := \mathbf{p}/\hbar$ is the initial wavevector of the incident neutron, $\mathbf{k}' := \mathbf{p}'/\hbar$ is the scattered wavevector of the outgoing neutron, and $\mathbf{Q} = \Delta\mathbf{p}/\hbar$ is a wavevector that represents a property in the lattice (translational symmetry or spin correlations). With the scattering of the neutron, there is also an energy transfer,

$$\Delta E = \hbar\omega = \frac{\hbar^2}{2m}(k^2 - k'^2), \quad (2.4)$$

where ω is the angular time-frequency, and m is the mass of a neutron [75]. There are two types of signals that are relevant for the types of scattering, structural wavevectors, and magnetic ordering wavevectors. Structural peaks happen when $\mathbf{Q} = \mathbf{G}$ for reciprocal

lattice wavevector $\mathbf{G}$, due to neutrons gaining crystal momentum from interactions with the samples' particles. Magnetic peaks happen when $\mathbf{Q} = \mathbf{q}_{\text{mag}} + \mathbf{G}$, where $\mathbf{q}_{\text{mag}}$ is a magnetic wavevector in the lattice that is detected due to interactions of the neutron beam with the samples' spins. Consider a beam of neutrons being fired at the lattice sample, as in Fig. 2.1. if increasing the cross section of the beam from σ to $\sigma + d\sigma$ leads to the solid angle of the scattered beam to increase from Ω to $\Omega + d\Omega$, with the energy of neutrons in the beam going from $\hbar\omega$ to $\hbar(\omega + d\omega)$ for a beam with momentum transfer $\mathbf{Q}$, then the scattering obeys the following equation

$$\frac{d^2\sigma}{d\Omega dE} = r_0^2 \frac{k'}{k} |F(\mathbf{Q})|^2 e^{-2W(\mathbf{Q})} \sum_{\mu, \nu} \left(\delta_{\nu\mu} - \frac{Q_\nu Q_\mu}{Q^2} \right) S^{\nu\mu}(\mathbf{Q}, \omega). \quad (2.5)$$

$r_0 \sim 10^{-15}$ m is the scattering radius, which depends on the material of the sample. $F(Q)$ is the atomic form factor. $e^{-2W(\mathbf{Q})}$ is the Debye-Waller factor, where $W(\mathbf{Q})$ corresponds to the thermal fluctuations of the positions of sites in the lattice [32, 75, 76]. $S^{\nu\mu}(\mathbf{Q}, \omega)$ is the dynamical structure factor between the spin components ν and μ , which can be expressed as

$$S^{\nu\mu}(\mathbf{Q}, \omega) = \frac{1}{2\pi\hbar} \sum_{j, j'} \int_{-\infty}^{\infty} e^{i\mathbf{Q} \cdot (\mathbf{R}_j - \mathbf{R}_{j'})} \langle s_j^\nu(0) s_{j'}^\mu(t) \rangle e^{-i\omega t} dt, \quad (2.6)$$

which is the Fourier transform of correlation between ν and μ components of spins across time and space. In the static case, such as systems in equilibrium with negligible fluctuations in the expectation values in time, $\langle s_j^\nu(0) s_{j'}^\mu(t) \rangle = \langle s_j^\nu(0) s_{j'}^\mu(0) \rangle$, which means that the static case of Eq. (2.6) is

$$S^{\nu\mu}(\mathbf{Q}, \omega) \propto S^{\nu\mu}(\mathbf{Q}) \delta(\omega), \quad (2.7)$$

where

$$S^{\nu\mu}(\mathbf{Q}) = \sum_{j, j'} e^{i\mathbf{Q} \cdot (\mathbf{R}_j - \mathbf{R}_{j'})} \langle s_j^\nu s_{j'}^\mu \rangle, \quad (2.8)$$

with $\langle s_j^\nu s_{j'}^\mu \rangle$ being the spatial (but not temporal) spin-spin correlations [77]. Assuming elastic scattering, then $\Delta E = 0$ in Eq. (2.4), which means that $k' = k \Rightarrow \frac{k'}{k} = 1$. Substituting this along with Eq. (2.7) into Eq. (2.6) gives the elastic neutron scattering differential cross-section:

$$\frac{d\sigma}{d\Omega} \propto |F(\mathbf{Q})|^2 \sum_{\nu,\mu} \left(\delta_{\nu\mu} - \frac{Q_\nu Q_\mu}{Q^2} \right) S^{\nu\mu}(\mathbf{Q}). \quad (2.9)$$

Defining the Fourier transform of the spins

$$\mathbf{s}(\mathbf{Q}) = \sum_j e^{-i\mathbf{Q}\cdot\mathbf{R}_j} \mathbf{S}_j \quad (2.10)$$

along with Eq. (2.8), allows for the structure factor to be expressed as

$$S^{\nu\mu}(\mathbf{Q}) = \langle s^\nu(\mathbf{Q}) s^\mu(-\mathbf{Q}) \rangle. \quad (2.11)$$

Thus, Eqs.(2.9), (2.10) and (2.11) relate the spin-spin correlations with the structure factor and the experimentally measurable neutron scattering cross-section.

Isotropic Spin Hamiltonian

Consider the following expectation value,

$$\langle s_j^\nu s_{j'}^\mu \rangle = \frac{\int_{\text{states } \mathcal{M}} s_j^\nu s_{j'}^\mu e^{-\beta\mathcal{H}(\mathcal{M})}}{\int_{\text{states } \mathcal{M}} e^{-\beta\mathcal{H}(\mathcal{M})}}. \quad (2.12)$$

The Heisenberg Hamiltonian $\mathcal{H} = \frac{1}{2} \sum_{jj'} J_{jj'} \mathbf{S}_j \cdot \mathbf{S}_{j'}$ is invariant under swapping of components in spins $\nu \leftrightarrow \mu$. Due to this isotropy, one can reindex the components with $\nu \leftrightarrow \mu$ in every site for every state without changing the Boltzmann weights, $e^{-\beta\mathcal{H}}$, thus

$$\int_{\text{states } \mathcal{M}} s_j^\nu s_{j'}^\mu e^{-\beta\mathcal{H}(\mathcal{M})} = \int_{\text{states } \mathcal{M}} s_j^\mu s_{j'}^\nu e^{-\beta\mathcal{H}(\mathcal{M})}, \quad (2.13)$$

which means that

$$\langle s_j^\nu s_{j'}^\mu \rangle = \langle s_j^\mu s_{j'}^\nu \rangle. \quad (2.14)$$

Another property of the Heisenberg Hamiltonian is invariance under global rotation of spins, i.e. if $\mathbf{S}_j \rightarrow \mathcal{R}\mathbf{S}_j$ for any rotation matrix $\mathcal{R}$ that is globally applied on all spins.

This means that for any $\nu, \mu \in \{x, y, z\}$ where $\nu \neq \mu$, one can rotate the spins by 90° in the ν - μ plane without changing the Hamiltonian:

$$\begin{aligned} s_j^\nu &\rightarrow s_j^\mu, \\ s_j^\mu &\rightarrow -s_j^\nu \quad \forall j. \end{aligned} \quad (2.15)$$

This rotation does not change the Hamiltonian and thus keeps the same Boltzmann weights and the expectation values. This means that

$$\langle s_j^\nu s_{j'}^\mu \rangle = \langle s_j^\mu (-s_{j'}^\nu) \rangle, \quad (2.16)$$

and thus

$$\langle s_j^\nu s_{j'}^\mu \rangle = -\langle s_j^\mu s_{j'}^\nu \rangle, \quad \forall j, j' \text{ if } \nu \neq \mu. \quad (2.17)$$

Combining this with Eq. (2.14) means that

$$\langle s_j^\nu s_{j'}^\mu \rangle = 0 \quad \forall j, j' \text{ if } \nu \neq \mu. \quad (2.18)$$

For the case where $\nu = \mu$, one can utilize Eq. (2.14) along with the rotational invariance of the Hamiltonian to show that

$$\langle s_j^x s_{j'}^x \rangle = \langle s_j^y s_{j'}^y \rangle = \langle s_j^z s_{j'}^z \rangle = \frac{1}{3} \langle \mathbf{S}_j \cdot \mathbf{S}_{j'} \rangle. \quad (2.19)$$

By Fourier transforming the spin correlations in accordance with Eq. (2.8), one can see that

$$S^{\nu\mu}(\mathbf{Q}) = \delta_{\nu\mu} S(\mathbf{Q}), \quad (2.20)$$

for Heisenberg model, which is the model used for $\text{CuAlCr}_4\text{S}_8$ (defined in Section 1.3), Eq. (2.20) can be substituted into Eq. (2.9) to give

$$\frac{d\sigma}{d\Omega}(\mathbf{Q}) \propto |F(\mathbf{Q})|^2 S(\mathbf{Q}). \quad (2.21)$$

Thus, for systems with isotropic spin interactions such as Heisenberg model, with elastic neutron scattering, the neutron-scattering structure factor is directly proportional to the differential cross section. This makes the structure factor a directly measurable quantity if a single-crystal sample and a neutron beam are present.

A property of neutron scattering that has not been discussed is polarization. Polarization divides the scattering cross section into spin-flipped neutrons and non-spin-flipped neutrons. From the relations between spin correlations and the polarization of scattered neutrons [78], the spin-spin structure factor for spin-flipped neutrons and non-spin-flipped neutrons are proportional to each other in isotropic spins, and thus polarization can be neglected in the Heisenberg model.

2.1.2 Specific Heat

Although spin-spin correlations are perhaps the physical measurements that are drawing the most attention in the study of $\text{CuAlCr}_4\text{S}_8$, it is important to look at other physical variables to understand the nature of the possible temperature-driven phase transitions. Phase transitions represent boundaries between different regimes with different spin-spin correlations, and temperature-driven phase transitions can be detected by investigating the heat capacity or specific heat. Given the equation for the partition function

$$\mathcal{Z} = \sum_{\text{state } \mathcal{M}} \exp[-\beta \mathcal{H}(\mathcal{M})], \quad (2.22)$$

then the expectation energy is

$$\langle E \rangle := \langle \mathcal{H} \rangle = \frac{\sum_{\text{state } \mathcal{M}} \mathcal{H} \exp[-\beta \mathcal{H}(\mathcal{M})]}{\mathcal{Z}}. \quad (2.23)$$

The second moment of energy is

$$\langle E^2 \rangle = \frac{\sum_{\text{state } \mathcal{M}} \mathcal{H}^2 \exp[-\beta \mathcal{H}(\mathcal{M})]}{\mathcal{Z}}. \quad (2.24)$$

One could use a general formula for the n^{th} moment of energy to express Eqs. (2.23) and (2.24):

$$\langle E^n \rangle = \frac{(-1)^n}{\mathcal{Z}} \frac{\partial^n \mathcal{Z}}{\partial \beta^n}. \quad (2.25)$$

Using this property, along with the definition of specific heat

$$c_V = \frac{1}{N_s} \frac{\partial \langle E \rangle}{\partial T}, \quad (2.26)$$

and recalling $\beta = 1/T$ for change of variables, combining Eq. (2.25) and (2.26) gives

$$c_V = \frac{1}{N_s T^2} (\langle E^2 \rangle - \langle E \rangle^2). \quad (2.27)$$

This means that the specific heat can be calculated by sampling the first and second moments of energy, rather than computing the numerical derivative of energy-versus-temperature data.

2.1.3 Susceptibility

For the susceptibility, we add a field term to the Hamiltonian

$$\mathcal{H} = \frac{1}{2} \sum_{jj'} \mathcal{J}_{jj'} \mathbf{S}_j \cdot \mathbf{S}_{j'} - \sum_j \mathbf{h}_j \cdot \mathbf{S}_j \quad (2.28)$$

or with a homogeneous field

$$\mathcal{H} = \frac{1}{2} \sum_{jj'} \mathcal{J}_{jj'} \mathbf{S}_j \cdot \mathbf{S}_{j'} - \mathbf{h} \cdot \mathbf{M}, \quad (2.29)$$

where

$$\mathbf{M} = \sum_j \mathbf{S}_j. \quad (2.30)$$

Let $\mathbf{h}$ be parallel to the magnetization, $\mathbf{h} = h\hat{M}$, then Eq. (2.29) can be written as

$$\mathcal{H} = \frac{1}{2} \sum_{ij} \mathcal{J}_{ij} \mathbf{S}_i \cdot \mathbf{S}_j - hM. \quad (2.31)$$

Note that the n^{th} moment of the modulus of the total magnetization, $M := \|\mathbf{M}\|$, is

$$\langle M^n \rangle = \frac{\sum_{\text{state } \mathcal{M}} M^n e^{-\mathcal{H}(\mathcal{M})}}{\mathcal{Z}}. \quad (2.32)$$

Eq. (2.32) can be expressed in terms of derivative of partition function as

$$\langle M^n \rangle = \frac{(-1)^n}{\beta^n \mathcal{Z}} \frac{\partial^n \mathcal{Z}}{\partial h^n}. \quad (2.33)$$

Noting that the uniform parallel-field susceptibility is

$$\chi = \frac{\partial \langle M \rangle}{\partial h}, \quad (2.34)$$

then using Eq. (2.33) and Eq. (2.34) gives

$$\chi = \frac{1}{N_s T} (\langle M^2 \rangle - \langle M \rangle^2). \quad (2.35)$$

Calculating the susceptibility from the variance of the magnetization as per Eq. (2.35) is useful in numerical methods such as Monte Carlo simulations.

Curie Weiss Temperature

Curie-Weiss temperature is defined from response of magnetization to field at high temperatures, where the system can be approximated to be paramagnetic [16]. For spins that have moduli S , the mean magnetization by Curie's law is

$$\mathbf{M} = \frac{S^2}{3T}(\mathbf{h} + \mathbf{h}_{\text{eff}}) \quad (2.36)$$

where

$$\mathbf{h}_{\text{eff}} = \sum_j \mathcal{J}_{ij} \mathbf{M} \quad (2.37)$$

is the effective mean field due to internal interactions. Plugging Eq. (2.37) into Eq. (2.36) gives

$$\mathbf{M} = \left(T - \frac{S^2}{3} \sum_j \mathcal{J}_{ij} \right)^{-1} \frac{S^2}{3} \mathbf{h} \quad (2.38)$$

This means that the parallel-field susceptibility in the paramagnetic regime is

$$\begin{aligned} \chi_{\text{MF}} &= \frac{\partial M}{\partial h_{\parallel}} \\ &= \left(T - \frac{S^2}{3} \sum_j \mathcal{J}_{ij} \right)^{-1} \frac{S^2}{3} \\ &\propto (T - \Theta_{\text{CW}})^{-1}, \end{aligned} \quad (2.39)$$

where

$$\Theta_{\text{CW}} = -\frac{S^2}{3} \sum_j \mathcal{J}_{ij} \quad (2.40)$$

is the Curie-Weiss temperature. Note that in our sign convention, $\mathcal{J}_{jj'} > 0$ for antiferromagnetic couplings, which means that systems with dominant antiferromagnetic couplings have negative Curie-Weiss temperatures. The Curie-Weiss temperature along with the critical temperature T_{C} , is a key quantity in assessing a system's frustration coefficient

$$f = -\Theta_{\text{CW}}/T_{\text{C}}, \quad (2.41)$$

where highly-frustrated systems tend to have a large positive frustration coefficient $f \gg 1$ [79]. This is the case since frustration inhibits ordering, resulting in the system having an ordering mechanism that is more vulnerable to thermal fluctuations and thus resulting in a lower critical temperature when compared to the Curie-Weiss temperature. Since the Curie-Weiss temperature can be obtained from susceptibility at high temperatures, probing the susceptibility at high temperatures is useful for analyzing the frustration of the system. Measuring the Curie-Weiss temperature also allows for verification of the exchange couplings used in the model, since the exchange couplings are expected to predict the Curie-Weiss temperature according to Eq. (2.40).

2.1.4 Spin-Spin Correlations

Rewriting the field term in (2.28) with Cartesian components of the field written explicitly,

$$\mathcal{H} = \frac{1}{2} \sum_{ij} \mathcal{J}_{jj'} \mathbf{S}_j \cdot \mathbf{S}_{j'} - \sum_{j,\nu} h_j^\nu s_j^\nu, \quad (2.42)$$

which gives the partition function

$$\mathcal{Z} = \sum_{\text{states } \mathcal{M}} \exp \left[-\beta \left(\frac{1}{2} \sum_{ij} \mathcal{J}_{jj'} \mathbf{S}_j \cdot \mathbf{S}_{j'} - \sum_{j,\nu} h_j^\nu s_j^\nu \right) \right]. \quad (2.43)$$

The spin-spin correlation between component ν of spin at site j and component μ of spin at j' can be expressed as

$$\langle s_j^\nu s_{j'}^\mu \rangle = \frac{1}{\beta^2 \mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial h_j^\nu \partial h_{j'}^\mu}. \quad (2.44)$$

Recall that the structure factor is related to the spin-spin correlations, being the Fourier transform

$$S^{\nu\mu}(\mathbf{Q}) = \sum_{j,j'} \langle s_j^\nu s_{j'}^\mu \rangle e^{-i\mathbf{Q} \cdot (\mathbf{R}_j - \mathbf{R}_{j'})}. \quad (2.45)$$

Thus, the spin-spin correlations are useful observables for calculating the neutron-scattering differential cross-section. In the zero-field case ($\mathbf{h}_j \equiv \mathbf{0}$), the Hamiltonian in Eq. (2.42) is isotropic, which means that

$$S^{\nu\mu}(\mathbf{Q}) = \delta_{\nu\mu} S(\mathbf{Q}). \quad (2.46)$$

2.1.5 Powder Average

Often times in experiments, rather than having a single crystal, the system being analyzed is a powder consisting of many tiny crystallites oriented in random directions. If the orientation of the crystallites is uniformly random, then a measurement of a scattered beam does not come from the contributions of a single wavevector, but instead from all wavevectors that have the same modulus. The powder average of the structure factor over all wavevectors with modulus $Q := \|\mathbf{Q}\|$ is defined as

$$\mathcal{S}(Q) = \frac{1}{4\pi} \int_0^{2\pi} \int_0^\pi d\phi d\theta \sin\theta S(\mathbf{q}), \quad (2.47)$$

where

$$\mathbf{q} = Q(\sin\theta \cos\phi, \sin\theta \sin\phi, \cos\theta). \quad (2.48)$$

Assuming elastic scattering,

$$\left(\frac{\partial \sigma}{\partial \Omega} \right)_{\text{powder}} = |F(Q)|^2 \mathcal{S}(Q), \quad (2.49)$$

where $F(Q)$ is the form factor of the scattering ions. The form factor arises from interference between the incident neutrons' wavevectors and the magnetic ions, which becomes significant at de Broglie wavelengths that are comparable to the magnetic ions' size. In the case of chromium spinels, the form factor for Cr^{3+} ions is defined as

$$\begin{aligned} F(Q) = & -0.3094e^{-0.0274\text{\AA}^2\left(\frac{Q}{4\pi}\right)^2} + 0.36804e^{-17.0355\text{\AA}^2\left(\frac{Q}{4\pi}\right)^2} \\ & + 0.6559e^{-6.5236\text{\AA}^2\left(\frac{Q}{4\pi}\right)^2} + 0.2856 \end{aligned} \quad (2.50)$$

according to Ref [4]. The integral in Eq (2.47) can be computed for MFT and large- N since both methods provide explicit functions for the structure factor $S(\mathbf{q})$ for any wavevector $\mathbf{q}$. For Monte Carlo, finite-size systems have a discrete set of possible wavevectors, and the integration for the powder average in momentum space requires the structure factor to be interpolated. At the time of writing this thesis, only large- N was used out of the classical methods to calculate the powder average for $\text{CuAlCr}_4\text{S}_8$.

2.2 Exchange Coupling Matrix

Analyzing the exchange coupling is useful for methods such as mean-field theory and large- N , which are showcased in the next sections. In the Heisenberg model with neighbour-dependent exchange coupling, the coupling coefficient can be expressed as

$$\mathcal{J}_{jj'}^{\nu\mu} = \sum_n \mathcal{A}_{jj'}^{(n)} J_n^{\nu\mu}, \quad (2.51)$$

where j, j' are site indices, ν, μ are spin components $\nu, \mu \in \{x, y, z\}$ and $\mathcal{A}_{jj'}^{(n)}$ is the adjacency matrix of n^{th} nearest neighbors meaning that

$$\mathcal{A}_{jj'}^{(n)} = \begin{cases} 1, & \text{if } j, j' \text{ are } n^{\text{th}} \text{ nearest neighbors.} \\ 0, & \text{otherwise.} \end{cases} \quad (2.52)$$

In the model for $\text{CuAlCr}_4\text{S}_8$, the neighbour indices are $n = \{1a, 1b, 2, 3a, 3b, 4, 5\}$, and the displacement between each neighbour type are presented in Appendix A. The $1a$ neighbours are pairs of sites that share an edge on a small tetrahedron, while the $1b$ neighbours are pairs of sites that share an edge on a large tetrahedron. The 2nd-nearest neighbours are sites that are separated by the next smallest euclidean after $1b$ -neighbours'. The $3a$ neighbours and $3b$ neighbours both correspond to the same Euclidean distance, but the $3a$ neighbours are separated by less tetrahedra edges than $3b$ neighbours are. The 4th and 5th nearest neighbours are the neighbours with the next smallest Euclidean distances, which unlike 3rd, are not divided into a and b classes since there are no variations in the number of tetrahedra edges between neighbours with indices 4 and 5. The Hamiltonian for spin systems segregated by n^{th} -neighbour interactions is

$$\mathcal{H} = \frac{1}{2} \sum_{jj'} \sum_n \mathcal{A}_{jj'}^{(n)} \left(\sum_{\nu\mu} J_n^{\nu\mu} s_j^\nu s_{j'}^\mu \right), \quad (2.53)$$

the $\frac{1}{2}$ factor is there to eliminate double counting. For the model used, we assume isotropy, $J_n^{\nu\mu} := J_n \delta_{\nu\mu}$, where the values of J_n are shown in Table 2.1. Thus, Eq. (2.53) becomes

$$\mathcal{H} = \frac{1}{2} \sum_{jj'} \sum_n \mathcal{A}_{jj'}^{(n)} J_n \left(\sum_\nu s_j^\nu s_{j'}^\nu \right). \quad (2.54)$$

Model	J_{1a} (K)	J_{1b} (K)	J_2 (K)	J_{3a} (K)	J_{3b} (K)	J_4 (K)	J_5 (K)
Up to J_{3b}	-0.2(2)	-2.7(2)	0.1(1)	6.0(1)	3.5(1)	0	0
Up to J_5	2.0(5)	-4.6(5)	1.1(3)	5.9(2)	3.3(2)	-1.0(2)	0.2(2)

Table 2.1: Two sets of exchange parameters, types of neighbours are sketched in Fig. 1.12. The up-to-3rd-NN parameters are obtained from a DFT fit which assumes that any neighbours further than $3b$ do not interact. The up-to-5th-NN parameters are fitted with the assumption that interaction are up to fifth-nearest-neighbour.

Note that the adjacency matrix definition $\mathcal{A}_{j,j'}^{(n)} := \mathcal{A}^{(n)}(\mathbf{R}_j, \mathbf{R}_{j'})$ where each site j is at position $\mathbf{R}_j$. Each site j can be re-indexed by a unit cell index I and a sublattice index c . With that definition, the Fourier transform of the adjacency Matrix $\mathcal{A}_{j,j'}^{(n)}$ is block-diagonal with blocks that can be indexed by the sublattice indices c, d and wavevector $\mathbf{q}$

$$\mathcal{A}_{cd}^{(n)}(\mathbf{q}) = \frac{1}{N_{\text{cell}}} \sum_{IH} \mathcal{A}^{(n)}(\mathbf{R}_I + \mathbf{r}_c, \mathbf{R}_H + \mathbf{r}_d) e^{-i\mathbf{q} \cdot (\mathbf{R}_{IH} + \mathbf{r}_{cd})}, \quad (2.55)$$

where $\mathbf{R}_{IH}$ is displacement between unit cells I and H , and $\mathbf{r}_{cd}$ is the displacement between sublattice sites c and d within the same unit cell. Due to the translational invariance of the lattice, $\mathcal{A}_{cd}^{(n)}(\mathbf{q})$ can be expressed as

$$\mathcal{A}_{cd}^{(n)}(\mathbf{q}) = \sum_I \mathcal{A}^{(n)}(\mathbf{r}_c, \mathbf{R}_I + \mathbf{r}_d) e^{-i\mathbf{q} \cdot (\mathbf{R}_I + \mathbf{r}_{cd})}, \quad (2.56)$$

Where $\mathbf{R}_I$ is the position of unit cell with index I . Meanwhile, the spins can be Fourier transformed for each sublattice index to give

$$\mathbf{s}_c(\mathbf{q}) = \sum_{I,c} \mathbf{S}_{I,c} e^{-i\mathbf{q} \cdot (\mathbf{R}_I + \mathbf{r}_c)} \quad (2.57)$$

where $\mathbf{R}_I + \mathbf{r}_c$ is the position of sublattice site c in unit cell I . Using Eqs. (2.56) and (2.57) to Fourier-transform the summand in Eq. (2.54), we can rewrite the Hamiltonian as

$$\mathcal{H} = \frac{1}{2} \sum_{\mathbf{q}} \sum_{c,d} \underbrace{\sum_n J_n \mathcal{A}_{cd}^{(n)}(\mathbf{q})}_{\mathcal{J}_{cd}(\mathbf{q})} \sum_{\nu} s_c^{\nu}(\mathbf{q}) s_d^{\mu}(-\mathbf{q}). \quad (2.58)$$

In the regular and breathing pyrochlore lattices, there are four sublattice sites. This means that we can set $c, d \in \{0, 1, 2, 3\}$. With the definition of adjacency matrices in momentum space, the Fourier transform of the exchange coupling can be expressed as

$$\mathcal{J}(\mathbf{q}) = \sum_k J_n \mathcal{A}^{(n)}(\mathbf{q}), \quad (2.59)$$

where $\mathcal{J}(\mathbf{q})$ is a 4×4 matrix for regular and breathing pyrochlore lattices. Since there are four sublattice sites, this explains that the Fourier transform block-diagonalizes the adjacency matrix into 4×4 blocks, as opposed to complete diagonalization that takes place in Bravais lattices. The Hamiltonian can be expressed in terms of wavevectors as

$$\mathcal{H} = \frac{1}{2} \sum_{\mathbf{q}} \sum_{c,d=1}^4 \underbrace{\mathcal{J}_{cd}(\mathbf{q}) \mathbf{s}_c(\mathbf{q}) \cdot \mathbf{s}_d(-\mathbf{q})}_{\{\mathcal{H}(\mathbf{q})\}_{cd}}. \quad (2.60)$$

By diagonalizing the 4×4 matrix $\mathcal{H}(\mathbf{q})$ for each $\mathbf{q}$, one can see that the eigenvalues of $\mathcal{J}(\mathbf{q})$ are proportional to the energy bands in momentum space, which are key quantities in analytical/semi-analytical methods such as mean field theory and large- N .

2.3 Mean Field Theory

2.3.1 Mean-Field Approximation

Assume spins are normalized such that $\|\mathbf{S}_j\| = 1$. Derivations are based on Refs. [46,80–82]. Consider the Hamiltonian

$$\mathcal{H} = \frac{1}{2} \sum_{j \neq j'} \sum_{\nu, \mu} \mathcal{J}_{jj'}^{\nu\mu} s_j^\nu s_{j'}^\mu - \sum_{j, \nu} h_j^\nu s_j^\nu, \quad (2.61)$$

where j, j' are site indices, and ν, μ are Cartesian component indices. A system can be defined by its density operator ρ , where $\rho(\mathcal{M})$ is the probability of the state of the system to be the state $\mathcal{M}$. The free energy functional for a given system with density operator ρ can be written as

$$\mathcal{F}_\rho = \langle \mathcal{H} \rangle - TS = \text{Tr}\{\rho \mathcal{H}\} + T \text{Tr}\{\rho \ln \rho\}, \quad (2.62)$$

where

$$\text{Tr} \equiv \sum_{\text{states } \mathcal{M}} \quad (2.63)$$

for states determined by degrees of freedom that take discrete values. If the degrees of freedom are instead continuous, then

$$\text{Tr} \equiv \int \left(\prod_j v_j \right) \quad (2.64)$$

where $\{v_j\}$ is the set of degrees of freedom in the system. For example, for a classical Heisenberg spin system with N_s sites, with $j = 1, \dots, N_s$, each spin

$\mathbf{S}_j = (\sin \theta_j \cos \phi_j, \sin \theta_j \sin \phi_j, \cos \theta_j)$ has two degrees of freedom; θ_j and ϕ_j . As a result, we have that for Eq. (2.64)

$$\text{Tr} \equiv \int_0^{2\pi} \prod_{j=1}^{N_s} d\phi_j \int_0^\pi \prod_{j=1}^{N_s} \sin \theta_j d\theta_j. \quad (2.65)$$

Solving (2.62) exactly would require us to find a density operator that minimizes $\mathcal{F}_\rho$. Finding the exact state whose density operator ρ minimizes $\mathcal{F}_\rho$ cannot be done analytically and requires heavy numerical calculations. Instead, mean-field theory (MFT) is invoked, where each spin site is treated as an independent spin in an external field. This means that the density operator can be factored out for the following approximate state,

$$\rho = \prod_j \rho_j(\mathbf{S}_j). \quad (2.66)$$

The density operator, ρ_j , on each site j , must satisfy

$$\text{Tr} \rho_j = 1, \quad (2.67)$$

and the average magnetization condition must be satisfied

$$\text{Tr} \rho_j \mathbf{S}_j = \langle \mathbf{S}_j \rangle, \quad (2.68)$$

where $\langle \mathbf{S}_j \rangle$ is the expectation value of the spin at site j . With these constraints, minimizing the variational free energy defined in Eq. (2.62) gives the mean-field solution. Including the constraints defined in Eq. (2.67) and Eq. (2.68) in the forms of Lagrange multipliers added to Eq. (2.62) gives

$$\begin{aligned} \mathcal{F}_\rho = & \text{Tr}\{\rho \mathcal{H}\} + T \text{Tr}\{\rho \ln \rho\} \\ & - T \text{Tr} \left\{ \sum_j [\lambda_j (\rho_j - 1) + (\rho_j \mathbf{S}_j - \langle \mathbf{S}_j \rangle) \cdot \mathbf{A}_j] \right\}, \end{aligned} \quad (2.69)$$

where λ_j and $\mathbf{A}_j$ are Lagrange multipliers for the constraints in Eq. (2.67) and Eq. (2.68), respectively. To minimize $\mathcal{F}_\rho$, we need to differentiate it. Define the single-site Hamiltonian

$$\mathcal{H}_j = \frac{1}{2} \sum_{j' \neq j} \sum_{\nu, \mu} \mathcal{J}_{jj'}^{\nu\mu} s_j^\nu s_{j'}^\mu - \sum_{\nu} h_j^\nu s_j^\nu. \quad (2.70)$$

Computing the functional derivatives of terms in Eq. (2.69) gives

$$\begin{aligned} \frac{\delta}{\delta \rho_j} \text{Tr}\{\rho \mathcal{H}\} &= \text{Tr}\{\mathcal{H}_j\} \\ \frac{\delta}{\delta \rho_j} \text{Tr}\{\rho \ln \rho\} &= \text{Tr} \ln \rho_j + \text{Tr}\{\mathbb{I}\}, \\ \frac{\delta}{\delta \rho_j} \text{Tr}\left\{\sum_j \lambda_j \rho_j\right\} &= \text{Tr}\{\lambda_j \mathbb{I}\}, \\ \frac{\delta}{\delta \rho_j} \text{Tr}\left\{\sum_j \rho_j \mathbf{S}_j \cdot \mathbf{A}_j\right\} &= \text{Tr}\{\mathbf{S}_j \cdot \mathbf{A}_j\}, \end{aligned} \quad (2.71)$$

where $\mathbb{I}$ is the identity operator. To minimize the free energy, we need $\delta \mathcal{F}_\rho / \delta \rho_j = 0$. Using the derivatives listed in Eq. (2.71) along with the expression for $\mathcal{F}_\rho$ in Eq. (2.69), then minimizing the free energy gives the constraint

$$0 = \frac{\delta \mathcal{F}_\rho}{\delta \rho_j} = \text{Tr}\{\mathcal{H}_j\} + T \text{Tr}\{\ln \rho_j + (1 - \lambda_j) \mathbb{I} - \mathbf{S}_j \cdot \mathbf{A}_j\}. \quad (2.72)$$

$\text{Tr}\{\mathcal{H}_j\} = 0$ for $\mathcal{H}_j$ in Eq.(2.70) since all the possible states' $\mathcal{H}_j$ values cancel each other out in the trace. The reason for that is, for every possible state with spin $\mathbf{S}_j$ at site j , there is another possible state with spin $-\mathbf{S}_j$ at site j , which is a pair of states that have opposite $\mathcal{H}_j$ values that cancel each other out according to Eq.(2.70). Thus,

$$\text{Tr}\{\mathcal{H}_j\} = 0. \quad (2.73)$$

Substituting Eq.(2.73) into Eq. (2.72) gives

$$0 = \text{Tr}\{\ln \rho_j + (1 - \lambda_j) \mathbb{I} - \mathbf{S}_j \cdot \mathbf{A}_j\}. \quad (2.74)$$

Dropping the trace in Eq. (2.74) gives

$$\ln \rho_j + (1 - \lambda_j) - \mathbf{S}_j \cdot \mathbf{A}_j = 0, \quad (2.75)$$

which leads us to an expression for the local density operator

$$\rho_j = e^{\lambda_j - 1} e^{\mathbf{A}_j \cdot \mathbf{S}_j}. \quad (2.76)$$

Substituting Eq. (2.76) into the constraint in Eq. (2.67),

$$e^{\lambda_j - 1} = 1 / \text{Tr}\{e^{\mathbf{A}_j \cdot \mathbf{S}_j}\}. \quad (2.77)$$

Combining Eqs. (2.76)-(2.77) gives

$$\rho_j = \frac{e^{\mathbf{A}_j \cdot \mathbf{S}_j}}{\text{Tr}\{e^{\mathbf{A}_j \cdot \mathbf{S}_j}\}}. \quad (2.78)$$

Noting the relation in Eq. (2.77), define the single-site partition function as

$$\mathcal{Z}_j = \text{Tr}\{e^{\mathbf{A}_j \cdot \mathbf{S}_j}\} = e^{1 - \lambda_j}. \quad (2.79)$$

With these solutions to the density operator, we solve for the free energy from Eq. (2.62). The terms in that equation can be solved by using Eqs.(2.67), (2.68) and (2.79) to give

$$\text{Tr}\{\rho \mathcal{H}\} = \frac{1}{2} \sum_{j,j',\nu,\mu} \mathcal{J}_{jj'}^{\nu\mu} \langle s_j^\nu \rangle \langle s_{j'}^\mu \rangle - \sum_{j,\nu} h_j^\nu \langle s_j^\nu \rangle, \quad (2.80)$$

$$\text{Tr}\{\rho \ln \rho\} = \sum_j (\mathbf{A}_j \cdot \langle \mathbf{S}_j \rangle - \ln \mathcal{Z}_j). \quad (2.81)$$

Substituting Eq. (2.80) and Eq. (2.81) into Eq. (2.62) gives

$$\begin{aligned} \mathcal{F}_\rho &= \frac{1}{2} \sum_{j,j',\nu,\mu} \mathcal{J}_{jj'}^{\nu\mu} \langle s_j^\nu \rangle \langle s_{j'}^\mu \rangle \\ &\quad - \sum_{j,\nu} h_j^\nu \langle s_j^\nu \rangle + T \sum_j (\mathbf{A}_j \cdot \langle \mathbf{S}_j \rangle - \ln \mathcal{Z}_j). \end{aligned} \quad (2.82)$$

Noting that the spin at site j is

$$\mathbf{S}_j = (\sin \theta_j \cos \phi_j, \sin \theta_j \sin \phi_j, \cos \theta_j). \quad (2.83)$$

Then, the expectation value of the spin at site j is

$$\langle \mathbf{S}_j \rangle = \text{Tr}\{\rho \mathbf{S}_j\} = \frac{\text{Tr}\{\rho_j \mathbf{S}_j\}}{\text{Tr}\{\rho_j\}} = \frac{\int_0^{2\pi} \int_0^\pi d\phi_j d\theta_j \sin \theta_j \mathbf{S}_j e^{\mathbf{A}_j \cdot \mathbf{S}_j}}{\int_0^{2\pi} \int_0^\pi d\phi_j d\theta_j \sin \theta_j e^{\mathbf{A}_j \cdot \mathbf{S}_j}}. \quad (2.84)$$

The integrals can be evaluated by utilizing the rotational invariance of the dot product to rotate the system such that $\mathbf{A}_j = A_j \hat{z}$ points in the $\hat{z}$ direction, which makes the integrals solvable, and give the following relation to first-order in $\mathbf{A}_j$:

$$\langle \mathbf{S}_j \rangle = \frac{1}{3} \mathbf{A}_j. \quad (2.85)$$

Note that $\mathbf{A}_j \propto 1/T$, and thus the neglect of higher-orders of $\mathbf{A}_j$ is a valid approximation for high temperatures. Note that Eq. (2.85) is the result for MFT on the Heisenberg model. In a model where the spins are still classical but have N components, one gets the relationship

$$\langle \mathbf{S}_j \rangle = \frac{1}{N} \mathbf{A}_j \quad (2.86)$$

instead of Eq. (2.85). Back to the Heisenberg model, the log of the single-site partition function, up to quadratic order in $\mathbf{A}_j$, is

$$\ln \mathcal{Z}_j = \ln \left[\int_0^\pi \int_0^{2\pi} d\phi_j d\theta_j e^{\mathbf{A}_j \cdot \mathbf{S}_j} \right] \approx \ln C + \frac{\|\mathbf{A}_j\|^2}{6}, \quad (2.87)$$

where C is a constant. Plugging Eqs.(2.87) and (2.86) into Eq. (2.82) gives

$$\begin{aligned} \mathcal{F}_\rho = & \frac{1}{2} \sum_{j,j',\nu,\mu} \mathcal{J}_{jj'}^{\nu\mu} \langle s_j^\nu \rangle \langle s_{j'}^\mu \rangle \\ & - \sum_{j,\nu} h_j^\nu \langle s_j^\nu \rangle + T \sum_j (3|\langle \mathbf{S}_j \rangle|^2 - \ln C - \frac{3}{2}|\langle \mathbf{S}_j \rangle|^2). \end{aligned} \quad (2.88)$$

This gives the mean-field free energy

$$\mathcal{F}_\rho = \frac{1}{2} \sum_{j,j',\nu,\mu} \langle s_j^\nu \rangle \{ 3T\delta_{jj'}\delta_{\nu\mu} + \mathcal{J}_{jj'}^{\nu\mu} \} \langle s_{j'}^\mu \rangle - \sum_{j,\nu} h_j^\nu \langle s_j^\nu \rangle - TN_s \ln C \quad (2.89)$$

2.3.2 Momentum Space

Taking Fourier transform block-diagonalizes the operators due to the discrete translational symmetry of the lattice. To demonstrate this, the site index j could be decomposed into lattice index I and sublattice index c . We introduce the Fourier transform of the spin and exchange couplings such that

$$s_{I,c}^\nu = \sum_{\mathbf{q}} s_c^\nu(\mathbf{q}) e^{i\mathbf{q} \cdot \mathbf{R}_{I,c}}, \quad (2.90)$$

$$\mathcal{J}_{IH,cd}^{\nu\mu} = \frac{1}{N_{\text{cell}}} \sum_{\mathbf{q}} \mathcal{J}_{cd}^{\nu\mu}(\mathbf{q}) e^{i\mathbf{q} \cdot \mathbf{R}_{IH,cd}}, \quad (2.91)$$

where N_{cell} is the number of unit cells, $\mathbf{R}_{I,c}$ is the position of sublattice c in unit cell I , $\mathbf{R}_{IH,cd} := \mathbf{R}_{H,d} - \mathbf{R}_{I,c}$, and the summation over $\mathbf{q}$ is over all the wavevectors in the Brillouin zone. Substituting Eqs.(2.90) and (2.91) into Eq. (2.89) gives the free energy in momentum space:

$$\begin{aligned} \mathcal{F}_\rho &= \frac{1}{2} \sum_{\mathbf{q}, c, d, \nu, \mu} s_c^\nu(\mathbf{q}) (NT \delta_{cd} \delta_{\nu\mu} + \mathcal{J}_{cd}^{\nu\mu}(\mathbf{q})) s_d^\mu(-\mathbf{q}) \\ &\quad - \sum_{\mathbf{q}, c, d, \nu, \mu} \delta_{cd} \delta_{\nu\mu} h_c^\nu(\mathbf{q}) s_d^\mu(-\mathbf{q}) - TN_s \ln C. \end{aligned} \quad (2.92)$$

Let $U_{c,\alpha}^{\nu,\mu}$ be a matrix such that

$$\sum_{d=1}^4 \sum_{\gamma=1}^3 \mathcal{J}_{c,d}^{\nu,\gamma} U_{d,\alpha}^{\gamma,\mu} = \varepsilon_\alpha U_{c,\alpha}^{\nu,\mu}, \quad (2.93)$$

then let

$$s_a^\nu(\mathbf{q}) = \sum_{\alpha} \sum_{\mu=1}^3 U_{\nu,\mu}^{a,\alpha}(\mathbf{q}) \phi_\alpha^\mu(\mathbf{q}), \quad (2.94)$$

and let

$$\tilde{h}_\alpha^\mu(\mathbf{q}) = \frac{1}{T} \sum_{a,\nu} h_a^\nu(\mathbf{q}) U_{\nu,\mu}^{a,\alpha}. \quad (2.95)$$

The expression for the free energy in terms of the normal mode amplitudes in momentum space is

$$\begin{aligned} \mathcal{F}_\rho &= \frac{1}{2} \sum_{\mathbf{q}, \alpha, \mu} \phi_\alpha^\mu(\mathbf{q}) (3T + \varepsilon_\alpha^\mu(\mathbf{q})) \phi_\alpha^\mu(-\mathbf{q}) \\ &\quad - T \sum_{\mathbf{q}, \alpha, \mu} \tilde{h}_\alpha^\mu(\mathbf{q}) \phi_\alpha^\mu(-\mathbf{q}) - TN_s \ln C. \end{aligned} \quad (2.96)$$

This introduces the degrees of freedom, $\{\phi_{a,\mathbf{q}}^\mu\}$, thus

$$\text{Tr} \equiv \int_{-\infty}^{+\infty} \prod_{\mathbf{q},\alpha,\mu} d\phi_{\mathbf{q},\alpha}^\mu. \quad (2.97)$$

Expressing the partition function as

$$\mathcal{Z} = \text{Tr} \exp\{-\mathcal{F}_\rho/T\}, \quad (2.98)$$

$\mathcal{Z}$ becomes a product of Gaussian integrals of the form.

$$\int_{-\infty}^{+\infty} d\phi e^{-\frac{1}{2}A\phi^2+B\phi} = \sqrt{\frac{2\pi}{A}} e^{\frac{B^2}{2A}}. \quad (2.99)$$

Using Eqs.(2.96)-(2.99), the partition function can be rewritten as

$$\mathcal{Z} = \prod_{\mathbf{q},\alpha,\mu} \left\{ \left[\frac{2\pi}{3 + \varepsilon_\alpha^\mu(\mathbf{q})/T} \right]^{1/2} e^{|\tilde{h}_{\mathbf{q},\alpha}^\mu|^2/[2(3+\varepsilon_\alpha^\mu(\mathbf{q})/T)]} \right\}. \quad (2.100)$$

From that partition function, the correlations between the normal modes can then be written as

$$\begin{aligned} \langle \phi_\alpha^\nu(\mathbf{q}) \phi_\gamma^\mu(\mathbf{q}') \rangle &= \frac{1}{\mathcal{Z}} \frac{\partial^2 \mathcal{Z}}{\partial \tilde{h}_{\mathbf{q},\alpha}^\nu \partial \tilde{h}_{\mathbf{q}',\gamma}^\mu} \bigg|_{\tilde{\mathbf{h}}=0} \\ &= \frac{\delta_{\mathbf{q},-\mathbf{q}'} \delta_{\alpha,\gamma} \delta_{\mu,\nu}}{3 + \varepsilon_\alpha^\mu(\mathbf{q})/T}. \end{aligned} \quad (2.101)$$

Using Eq. (2.94), the Fourier transform of the spins can be expressed in terms of normal modes:

$$s_c^\nu(\mathbf{q}) s_d^\mu(-\mathbf{q}) = \left(\sum_{\alpha,\gamma=1}^4 \sum_{\nu',\mu'=1}^3 U_{\nu,\nu'}^{c,\alpha}(\mathbf{q}) \phi_\alpha^{\nu'}(\mathbf{q}) U_{\mu,\mu'}^{d,\gamma}(-\mathbf{q}) \phi_\gamma^{\mu'}(-\mathbf{q}) \right), \quad (2.102)$$

which gives

$$\langle s_c^\nu(\mathbf{q}) s_d^\mu(-\mathbf{q}) \rangle = \left(\sum_{\alpha,\gamma=1}^4 \sum_{\nu',\mu'=1}^3 U_{\nu,\nu'}^{c,\alpha}(\mathbf{q}) U_{\mu,\mu'}^{d,\gamma}(-\mathbf{q}) \langle \phi_\gamma^{\mu'}(\mathbf{q}) \phi_\alpha^{\nu'}(-\mathbf{q}) \rangle \right). \quad (2.103)$$

Using Eq. (2.101),

$$\langle s_c^\nu(\mathbf{q}) s_d^\mu(-\mathbf{q}) \rangle = \left(\sum_{\alpha=1}^4 \sum_{\nu'=1}^3 \frac{U_{\nu,\nu'}^{c,\alpha}(\mathbf{q}) U_{\mu,\nu'}^{d,\alpha}(-\mathbf{q})}{3 + \varepsilon_\alpha^\nu(\mathbf{q})/T} \right). \quad (2.104)$$

For isotropic Heisenberg model $U_{\nu,\nu'}^{c,\alpha} \equiv U^{c,\alpha} \delta_{\nu\nu'}$. Since $\mathcal{J}_{\nu,\nu'}^{c,\alpha} \equiv \mathcal{J}^{c,\alpha} \delta_{\nu\nu'}$, and $\varepsilon_\alpha^\nu \equiv \varepsilon_\alpha$. Thus,

$$\langle s_c^\nu(\mathbf{q}) s_d^\mu(-\mathbf{q}) \rangle = \delta_{\nu\mu} \left(\sum_{\alpha=1}^4 \frac{U^{c,\alpha}(\mathbf{q}) U^{d,\alpha}(-\mathbf{q})}{3 + \varepsilon_\alpha(\mathbf{q})/T} \right). \quad (2.105)$$

The differential cross section for elastic scattering, from Eqs. (2.9) and (2.11), then reads

$$\frac{d\sigma}{d\Omega}(\mathbf{q}) \propto [F(\mathbf{q})]^2 \sum_{\nu,\mu} \left(\delta_{\nu\mu} - \frac{q_\nu q_\mu}{q^2} \right) \sum_{cd} \langle s_c^\nu(\mathbf{q}) s_d^\mu(-\mathbf{q}) \rangle, \quad (2.106)$$

which can be combined with Eq. (2.105) to give

$$\frac{d\sigma}{d\Omega}(\mathbf{q}) \propto [F(\mathbf{q})]^2 S(\mathbf{q}), \quad (2.107)$$

where

$$S(\mathbf{q}) = \sum_{c,d} \langle s_c^\nu(\mathbf{q}) s_d^\mu(-\mathbf{q}) \rangle = \sum_{c,d=1}^4 \left(\sum_{\alpha=1}^4 \frac{U^{c,\alpha}(\mathbf{q}) U^{d,\alpha}(-\mathbf{q})}{3 + \varepsilon_\alpha(\mathbf{q})/T} \right). \quad (2.108)$$

The critical temperature is estimated as the temperature at which the structure factor $S(\mathbf{q}^*)$ diverges for some wavevector $\mathbf{q}^*$. Let $\varepsilon_1(\mathbf{q})$ be the lowest eigenvalue of the 4×4 matrix $\mathcal{J}(\mathbf{q})$, then the critical temperature is

$$T_C^{\text{MF}} = -\frac{1}{3} \min_{\mathbf{q} \in \text{BZ}} (\varepsilon_1(\mathbf{q})). \quad (2.109)$$

At that temperature, the structure factor is expected to peak at the ordering wavevector(s), $\mathbf{q}^*$, that satisfy

$$\varepsilon_1(\mathbf{q}^*) = \min(\varepsilon_1(\mathbf{q})). \quad (2.110)$$

This means that the ordering wavevector(s) are the wavevectors of the spin configurations in the ground state(s). For spins that are normalized to have a modulus that is $\|\mathbf{S}_j\| = S$ rather than 1, the same partition function is obtained under the transformation $T \rightarrow TS^2$,

$\mathbf{S}_j \rightarrow S\mathbf{S}_j$. This scaling changes the critical temperature at which there is a singularity, meaning that the critical temperature for spins with modulus S is

$$T_C^{\text{MF}} = -\frac{S^2}{3} \min_{\mathbf{q} \in \text{BZ}}(\varepsilon_1(\mathbf{q})). \quad (2.111)$$

Since the derivation of the free energy is based on the high-temperature approximation in Eq. (2.87), the MFT approximation is expected to break down and become inaccurate at low temperatures. For that reason, T_C^{MF} is expected to deviate from the actual critical temperature of the system. While Eq. (2.108) is written in diagonal form to show the relationship between $\varepsilon_\alpha(\mathbf{q})$ and T_C^{MF} , it is also possible to rewrite the equation in terms of the original exchange coupling matrix, by noting that

$$\begin{aligned} & \sum_{\alpha=1}^4 \frac{U^{c,\alpha}(\mathbf{q})U^{d,\alpha}(-\mathbf{q})}{3 + \varepsilon_\alpha(\mathbf{q})/T} \\ &= \left\{ U(\mathbf{q}) \left[\beta \text{diag}(\varepsilon_1(\mathbf{q}), \dots, \varepsilon_4(\mathbf{q})) + 3\mathbb{I}_{4 \times 4} \right] [U(\mathbf{q})]^\dagger \right\}_{cd} \\ &= \left\{ (\beta \mathcal{J}(\mathbf{q}) + 3)^{-1} \right\}_{cd}. \end{aligned} \quad (2.112)$$

Substituting this into Eq. (2.108) gives

$$S(\mathbf{q}) = \sum_{c,d=1}^4 \left\{ (\mathcal{J}(\mathbf{q})/T + 3/S^2)^{-1} \right\}_{cd}. \quad (2.113)$$

For systems where the classical spins have N components and moduli S , the MFT structure factor becomes

$$S(\mathbf{q}) \propto \sum_{c,d=1}^4 \left\{ (\mathcal{J}(\mathbf{q})/T + N/S^2)^{-1} \right\}_{cd}, \quad (2.114)$$

and the MFT critical temperature becomes

$$T_C^{\text{MF}} = -\frac{S^2}{N} \min_{\mathbf{q} \in \text{BZ}}(\varepsilon_1(\mathbf{q})), \quad (2.115)$$

where $N = 3$ for Heisenberg model, 1 for Ising model [81, 82].

2.4 Large- N

2.4.1 Quadratic Approximation of Free Energy

The derivation below is based on [83, 84]. Due to the isotropy of the Heisenberg model, we have $\mathcal{J}_{jj'}^{\nu\mu} = J_{jj'}\delta_{\nu\mu}$. There is also the classical spin-norm constraint

$$\|\mathbf{S}_i\|^2 = S^2. \quad (2.116)$$

The partition function is

$$\mathcal{Z} = \int_{-\infty}^{+\infty} \prod_j \left(\prod_{\nu=1}^N ds_j^\nu \right) \delta(\|\mathbf{S}_j\|^2 - S^2) \exp \left(-\frac{\beta}{2} \sum_{jj'} \sum_{\nu=1}^N J_{jj'} s_j^\nu s_{j'}^\nu \right), \quad (2.117)$$

where the $\delta(\|\mathbf{S}_j\|^2 - S^2)$ factor restricts the spins to have moduli S . The delta function in Eq. (2.117) can be rewritten using

$$\delta(x) \propto \int_{\lambda-i\infty}^{\lambda+i\infty} d\xi e^{-\frac{\xi}{2}x}, \quad (2.118)$$

where λ is a real constant that will be determined later. While the Hamiltonian is quadratic with respect to the spins, the action has higher order terms when including the spin-norm constraint in Eq. (2.116). Restraining the spin norms requires high-order terms in the action, but restricting only the *average* norm of the spins results in a quadratic term in the action and thus can be used in analytical quadratic theory calculations.

$$\mathcal{Z} = \int_{\lambda-i\infty}^{\lambda+i\infty} \prod_j d\xi_j e^{-\frac{\xi_j}{2}(\|\mathbf{S}_j\|^2 - S^2)} \int_{-\infty}^{+\infty} \prod_i \prod_{\nu=1}^N ds_i^\nu \exp \left(-\frac{\beta}{2} \sum_{jj'} \sum_{\nu=1}^N J_{jj'} s_j^\nu s_{j'}^\nu \right). \quad (2.119)$$

Define $\int \mathcal{D}\mathbf{S} := \int_{-\infty}^{+\infty} \prod_{j=1}^{N_s} \prod_{\nu=1}^N ds_j^\nu$, and $\int \mathcal{D}\boldsymbol{\xi} := \int_{\lambda-i\infty}^{\lambda+i\infty} \prod_{j=1}^{N_s} d\xi_j$, then the partition function can be written as

$$\mathcal{Z} = \int \mathcal{D}\mathbf{S} \mathcal{D}\boldsymbol{\xi} \exp \left(\sum_{j=1}^{N_s} \frac{\xi_j}{2} S^2 - \frac{1}{2} \sum_{jj'}^{N_s} \sum_{\nu,\mu=1}^N \beta J_{jj'} + \xi_j \delta_{j,j'} \delta_{\nu\mu} s_j^\nu s_{j'}^\mu \right). \quad (2.120)$$

By defining the matrices

$$\begin{aligned} \mathbf{S}^\dagger &:= (s_1^1, s_1^2, \dots, s_2^1, s_2^2, \dots, s_{N_s}^1, s_{N_s}^2, \dots, s_{N_s}^{N-1}, s_{N_s}^N), \\ \mathcal{J}_{jj'}^{\nu\mu} &= J_{jj'} \delta_{\nu\mu}, \\ (\Lambda)_{jj'}^{\nu\mu} &= \xi_j \delta_{jj'} \delta_{\nu\mu}, \end{aligned} \quad (2.121)$$

the partition function can then be written as

$$\mathcal{Z} = \int \mathcal{D}\mathbf{S} \mathcal{D}\boldsymbol{\xi} \exp\left(\frac{S^2}{2N} \text{Tr}\Lambda\right) \exp\left(-\frac{1}{2} \mathbf{S}^\dagger (\beta\mathcal{J} + \Lambda) \mathbf{S}\right), \quad (2.122)$$

where

$$\text{Tr}\Lambda = \sum_{j,\nu} \Lambda_{jj}^{\nu\nu}. \quad (2.123)$$

for summation over sites j and Cartesian components ν . Computing the Gaussian integral over $\mathbf{S}$ in Eq. (2.122),

$$\mathcal{Z} = \int \mathcal{D}\boldsymbol{\xi} \exp\left(\frac{S^2}{2N} \text{Tr}\Lambda\right) \left(\frac{(2\pi)^{N_s N}}{\det(\beta\mathcal{J} + \Lambda)}\right)^{1/2}. \quad (2.124)$$

Ignoring the constant factor $(2\pi)^{N_s N}$, utilizing $\det A = \exp(\text{Tr}\{\ln A\})$, and letting $V = \beta\mathcal{J} + \Lambda$, Eq. (2.124) becomes

$$\begin{aligned} \mathcal{Z} &= \int \mathcal{D}\boldsymbol{\xi} \exp\left(\frac{S^2}{2N} \text{Tr}\Lambda\right) \exp\left(-\frac{1}{2} \text{Tr}\ln V\right) \\ &= \int \mathcal{D}\boldsymbol{\xi} \exp\left[\text{Tr}\left(\frac{S^2}{2N} \Lambda - \frac{1}{2} \ln V\right)\right]. \end{aligned} \quad (2.125)$$

Evaluating this multi-dimensional integral exactly is not straightforward. Instead, we approximate the integral using a saddle-point approximation.

$$\begin{aligned} \frac{\partial}{\partial \xi_k} \text{Tr}\left(\frac{S^2}{N} \Lambda - \ln V\right) &= 0 \\ \Rightarrow \text{Tr}\left(\frac{S^2}{N} \frac{\partial \Lambda}{\partial \xi_k}\right) - \text{Tr}\left(V^{-1} \frac{\partial V}{\partial \xi_k}\right) &= 0 \\ \Rightarrow \sum_{j,\nu} \frac{S^2}{N} \delta_{jk} - \sum_{j,j',\nu,\mu} (V^{-1})_{jj'}^{\nu\mu} \left(\frac{\partial V}{\partial \xi_k}\right)_{j'j}^{\mu\nu} &= 0 \end{aligned} \quad (2.126)$$

Note that $V_{jj'}^{\nu\mu} := V_{jj'} \delta_{\nu\mu} = (\beta J_{jj'} + \xi_j \delta_{jj'}) \delta_{\nu\mu}$. Utilizing translational invariance, let $\xi_j \equiv \lambda$ which is a Lagrange multiplier that only depends on temperature (or inverse-temperature

β). Plugging this into Eq. (2.126), and removing the indices for the Cartesian components ν, μ :

$$\begin{aligned}
S^2 - N \sum_{j,j'}^{N_s} (V^{-1})_{jj'} \left(\frac{\partial V}{\partial \lambda} \delta_{kj} \right)_{j'j} &= 0 \\
\Rightarrow S^2 - N \sum_{j,j'} (V^{-1})_{jj'} \delta_{jk} \delta_{jj'} &= 0 \\
\Rightarrow S^2 - N [(\beta \mathcal{J} + \xi)^{-1}]_{kk} \\
\Rightarrow \frac{S^2}{N} &= [(\beta \mathcal{J} + \xi)^{-1}]_{kk}.
\end{aligned} \tag{2.127}$$

Recalling that by translational invariance, $\Lambda = \lambda \mathbb{I}$ for the identity operator $\mathbb{I}$:

$$\frac{N_s S^2}{N} = \sum_k [(\beta \mathcal{J} + \lambda \mathbb{I})^{-1}]_{kk}, \tag{2.128}$$

where λ is the Lagrange multiplier that satisfies the average-spin-norm constraint in Eq. (2.128). The matrix $\mathcal{J}$ can be block-diagonalized into 4×4 blocks $\mathcal{J}(\mathbf{q})$ as per Eq. (2.91), where $\mathcal{J}(\mathbf{q})$ has eigenvalues $\{\varepsilon_\alpha(\mathbf{q}) | \alpha = 1, 2, 3, 4\}$. Thus, the diagonalized form of the trace in Eq. (2.128) is written as

$$\frac{N_s S^2}{N} = \sum_{\mathbf{q} \in \text{BZ}} \sum_{\alpha=1}^4 \frac{1}{\beta \varepsilon_\alpha(\mathbf{q}) + \lambda}, \tag{2.129}$$

where λ needs to be computed numerically, and $\text{BZ} = \{\frac{n_1}{L} \mathbf{b}_1 + \frac{n_2}{L} \mathbf{b}_2 + \frac{n_3}{L} \mathbf{b}_3 \mid n_1, n_2, n_3 = 0, \dots, L-1\}$ for a system with $L \times L \times L$ unit cells.

2.4.2 Ground-State Energy

Let

$$\varepsilon_{\text{g.s.}} = \min_{\mathbf{q} \in \text{BZ}} \{\varepsilon_1(\mathbf{q})\} \tag{2.130}$$

be the minimum eigenvalue of the exchange coupling $\mathcal{J}$, and let $\mathcal{W}_{\text{g.s.}}$ be the degeneracy of the ground-state energy. Taking Eq. (2.129) in the limit of $T \rightarrow 0$ which means

$\beta = 1/T \rightarrow \infty$, Then only ground states contribute. Thus, for $\beta \rightarrow \infty$,

$$\begin{aligned} \frac{N_s S^2}{N} &= \frac{\mathcal{W}_{\text{g.s.}}}{\beta \varepsilon_{\text{g.s.}} + \lambda} \\ \Rightarrow \quad \lambda &\rightarrow \frac{N \mathcal{W}_{\text{g.s.}}}{N_s S^2} - \beta \varepsilon_{\text{g.s.}}. \end{aligned} \quad (2.131)$$

We can find equations for $\partial\lambda/\partial\beta$ by differentiating Eq. (2.128) with respect to β :

$$0 = \sum_{\mathbf{q}} \sum_{\alpha} \frac{\varepsilon_{\alpha}(\mathbf{q}) + \partial\lambda/\partial\beta}{(\beta \varepsilon_{\alpha}(\mathbf{q}) + \lambda)^2}. \quad (2.132)$$

Again, taking the limit $\beta \rightarrow \infty$ and using the limit for λ in Eq. (2.131):

$$\begin{aligned} 0 &= \mathcal{W}_0 \left(\frac{\partial\lambda/\partial\beta}{(N \mathcal{W}_0 / (N_s S^2))^2} \right) \\ \Rightarrow \quad \frac{\partial\lambda}{\partial\beta} &= -\varepsilon_{\text{g.s.}}. \end{aligned} \quad (2.133)$$

Plugging Eqs.(2.131) and (2.133) into Eq. (2.145):

$$\lim_{T \rightarrow 0} \langle E \rangle = \frac{N_s S^2 \varepsilon_{\text{g.s.}}}{2}. \quad (2.134)$$

Thus the mean energy per site for a ground-state configuration is $\frac{S^2}{2} \varepsilon_{\text{g.s.}}$, where $\varepsilon_{\text{g.s.}}$ is the lowest eigenvalue of the exchange coupling matrix $\mathcal{J}$ (for the sign convention where antiferromagnetic coupling coefficients are positive).

2.4.3 Structure Factor

When an external field is included, the partition function becomes

$$\begin{aligned} \mathcal{Z} &= \int \mathcal{D}\mathbf{S} \mathcal{D}\mathbf{\xi} \exp \left(\frac{S^2}{2N} \sum_{j,j',\nu,\mu} \xi_j \delta_{jj'} \delta_{\nu\mu} - \frac{1}{2} \sum_{j,j',\nu,\mu} (\beta J_{jj'} + \xi_j \delta_{jj'}) \delta_{\nu\mu} s_j^{\nu} s_{j'}^{\mu} + \right. \\ &\quad \left. \sum_{j,\nu} h_j^{\nu} s_j^{\nu} \right). \end{aligned} \quad (2.135)$$

Defining $\mathbf{H}^\dagger := (h_1^1, h_1^2, \dots, h_2^1, h_2^2, \dots, h_{N_s}^1, h_{N_s}^2, \dots, h_{N_s}^{N-1}, h_{N_s}^N)$, the partition function can be written in matrix form as

$$\mathcal{Z} = \int \mathcal{D}\mathbf{S} \mathcal{D}\boldsymbol{\xi} \exp\left(\frac{S^2}{2N} \text{Tr}\Lambda\right) \exp\left(-\frac{1}{2} \mathbf{S}^\dagger (\beta\mathcal{J} + \Lambda) \mathbf{S} + \mathbf{H}^\dagger \mathbf{S}\right). \quad (2.136)$$

Using the multi-variable Gaussian integral property

$$\int d^n \mathbf{x} \exp(-\mathbf{x}^\dagger \mathbf{A} \mathbf{x} + \mathbf{b}^\dagger \mathbf{x}) = \sqrt{\frac{(2\pi)^n}{\det \mathbf{A}}} \exp\left(\frac{1}{2} \mathbf{b}^\dagger \mathbf{A}^{-1} \mathbf{b}\right) \quad (2.137)$$

to integrate out the spins $\mathcal{D}\mathbf{S}$ in Eq(2.136), we find

$$\mathcal{Z} = \int \mathcal{D}\boldsymbol{\xi} \exp\left(\frac{S^2}{2N} \text{Tr}\xi\right) \left(\frac{(2\pi)^{NN_s}}{\det(\beta\mathcal{J} + \Lambda)}\right)^{1/2} \exp\left[\frac{1}{2} \mathbf{H}^\dagger (\beta\mathcal{J} + \Lambda)^{-1} \mathbf{H}\right]. \quad (2.138)$$

Taking the saddle point integral:

$$\mathcal{Z} \approx \exp\left(\frac{N_s S^2}{2} \lambda\right) \left(\prod_{\mathbf{q}} \prod_{k=1}^4 \frac{1}{(\beta\varepsilon_k(\mathbf{q}) + \lambda)}\right)^{N/2} \exp\left[\frac{1}{2} \sum_{jj'\nu\mu} h_j^\nu [(\beta\mathcal{J} + \lambda)^{-1}]_{jj'}^{\nu\mu} h_{j'}^\mu\right]. \quad (2.139)$$

Note that for zero field, $\mathbf{H} = \mathbf{0}$, Eq. (2.139) gives us the same partition function as Eq. (2.125), which should mean we get the same $\Lambda_{jj'}^{\nu\mu} = \lambda \delta_{jj'} \delta_{\nu\mu}$ for λ dependent only on β . Noting that

$$\langle s_j^\nu s_{j'}^\mu \rangle = \frac{\int \mathcal{D}\mathbf{S} s_j^\nu s_{j'}^\mu e^{-\beta\mathcal{H}}}{\int \mathcal{D}\mathbf{S} e^{-\beta\mathcal{H}}} = \frac{1}{\mathcal{Z}} \frac{\partial^2 \mathcal{Z}}{\partial h_j^\nu \partial h_{j'}^\mu}, \quad (2.140)$$

then from the partition function in Eq. (2.139), we get

$$\langle s_j^\nu s_{j'}^\mu \rangle|_{\mathbf{H}=\mathbf{0}} = [(\beta\mathcal{J} + \lambda\mathbb{I})^{-1}]_{jj'}^{\nu\mu}. \quad (2.141)$$

Taking the Fourier transform

$$\begin{aligned} \langle s^\nu(\mathbf{q}) s^\mu(-\mathbf{q}) \rangle &= \frac{1}{N_{\text{cell}}} \sum_{j,j'} \langle s_j^\nu s_{j'}^\mu \rangle e^{i(\mathbf{R}_{j'} - \mathbf{R}_j) \cdot \mathbf{q}} = \\ &= \frac{1}{N_{\text{cell}}} \sum_{j,j'} [(\beta\mathcal{J} + \lambda\mathbb{I})^{-1}]_{jj'}^{\nu\mu} e^{i(\mathbf{R}_{j'} - \mathbf{R}_j) \cdot \mathbf{q}}. \end{aligned} \quad (2.142)$$

Using Eq. (2.91), to rewrite Eq. (2.142):

$$\langle s^\nu(\mathbf{q}) s^\mu(-\mathbf{q}) \rangle = \sum_{c,d=1}^4 [(\beta \mathcal{J}(\mathbf{q}) + \lambda \mathbb{I})^{-1}]_{cd}^{\nu\mu}, \quad (2.143)$$

where c, d are sublattice indices. The structure factor, $S(\mathbf{q})$, is then available as

$$\langle s^\nu(\mathbf{q}) s^\mu(-\mathbf{q}) \rangle = \delta_{\nu\mu} S(\mathbf{q}). \quad (2.144)$$

Note that the MFT structure factor, derived in Eq. (2.113), is a special case of the large- N structure factor, where $\lambda \equiv 3/S^2$.

2.4.4 Specific Heat

Using Eq. (2.139) along with $\langle E \rangle = -\frac{\partial \ln \mathcal{Z}}{\partial \beta}$ [from Eq. (2.25)], the expectation value of energy is

$$\langle E \rangle = -\frac{N_s S^2}{2} \frac{\partial \lambda}{\partial \beta} + \frac{N}{2} \sum_{\mathbf{q}} \sum_{\alpha=1}^4 \frac{\varepsilon_\alpha(\mathbf{q}) + \frac{\partial \lambda}{\partial \beta}}{\beta \varepsilon_\alpha(\mathbf{q}) + \lambda}. \quad (2.145)$$

The specific heat can then be obtain by plugging Eq. (2.145) into Eq. (2.26) to get

$$\begin{aligned} c_V &= \frac{1}{N_s T^2} \frac{\partial^2 \ln \mathcal{Z}}{\partial \beta^2} \\ &= \frac{1}{T^2} \left(\frac{S^2}{2} \frac{\partial^2 \lambda}{\partial \beta^2} + \frac{N}{2 N_s} \sum_{\mathbf{q}} \sum_{\alpha=1}^4 \left[\left(\frac{\varepsilon_\alpha(\mathbf{q}) + \partial \lambda / \partial \beta}{\beta \varepsilon_\alpha(\mathbf{q}) + \lambda} \right)^2 - \frac{\partial^2 \lambda / \partial \beta^2}{\beta \varepsilon_\alpha(\mathbf{q}) + \lambda} \right] \right). \end{aligned} \quad (2.146)$$

After solving for λ in Eq. (2.129), then $\partial \lambda / \partial \beta$ can be obtained from solving from the derivative of the constraint in (2.129) with respect to β , which is

$$0 = \sum_{\mathbf{q} \in \text{BZ}} \sum_{\alpha} \frac{\varepsilon_\alpha(\mathbf{q}) + \partial \lambda / \partial \beta}{(\beta \varepsilon_\alpha(\mathbf{q}) + \lambda)^2}. \quad (2.147)$$

Differentiating Eq. (2.147) introduces a constraint that involves $\partial^2 \lambda / \partial \beta^2$,

$$0 = \sum_{\mathbf{q}} \sum_{\alpha} \left[\frac{\partial^2 \lambda / \partial \beta^2}{(\beta \varepsilon_\alpha(\mathbf{q}) + \lambda)^2} - 2 \frac{(\varepsilon_\alpha(\mathbf{q}) + \partial \lambda / \partial \beta)^2}{(\beta \varepsilon_\alpha(\mathbf{q}) + \lambda)^3} \right]. \quad (2.148)$$

Thus, Eqs. (2.129), (2.147), and (2.148) can be used to solve for λ and its derivatives. λ and its derivatives, $d\lambda/d\beta$ and $d^2\lambda/d\beta^2$, are needed to calculate the large- N specific heat in Eq. (2.146).

2.4.5 Susceptibility

The susceptibility is assumed to be the uniform susceptibility, i.e., the susceptibility to a homogeneous field,

$$\chi = \frac{\partial}{\partial h} \langle |\sum_j \mathbf{S}_j| \rangle. \quad (2.149)$$

The susceptibility can be written as

$$\chi = \frac{\left\langle \left(\sum_j \mathbf{S}_j \right)^2 \right\rangle - \langle \sum_j \mathbf{S}_j \rangle^2}{N_s T}, \quad (2.150)$$

where

$$\langle \sum_j \mathbf{S}_j \rangle = 0 \quad (2.151)$$

due to rotational symmetry of the Heisenberg Hamiltonian, while

$$\begin{aligned} \left\langle \left(\sum_j \mathbf{S}_j \right)^2 \right\rangle &= \left\langle \sum_{\nu} \left(\sum_j s_j^{\nu} \right)^2 \right\rangle \\ &= \sum_{\nu} \sum_{jj'} \langle s_j^{\nu} s_{j'}^{\nu} \rangle \\ &= N_s S(\mathbf{q} = \mathbf{0}), \end{aligned} \quad (2.152)$$

where $S(\mathbf{q} = 0)$ is the structure factor for the zero wavevector. Plugging Eqs. (2.151) and (2.152) into Eq. (2.150) to get the large- N susceptibility:

$$\chi = \frac{S(\mathbf{q} = 0)}{T}. \quad (2.153)$$

2.4.6 Implementation

Constructing $\mathcal{J}(\mathbf{q})$

For a general non-Bravais lattice with Heisenberg exchange, the exchange coupling matrix in momentum space is the Fourier transform

$$\{\mathcal{J}(\mathbf{q})\}_{cd} = \frac{1}{N_{\text{cell}}} \sum_{IH} \mathcal{J}_{IH,cd} e^{-i\mathbf{q}\cdot\mathbf{R}_{IH,cd}}, \quad (2.154)$$

where I, H are unit cell indices, c, d are sublattice indices, N_{cell} is the number of unit cells, and $\mathcal{J}_{IH,cd}$ is the exchange coupling between the two sites. Due to translational invariance in the Hamiltonian, one can fix one of the unit cell indices, say I , and rewrite Eq. (2.154) as

$$\{\mathcal{J}(\mathbf{q})\}_{cd} = \sum_H \mathcal{J}_{IH,cd} e^{-i\mathbf{q}\cdot\mathbf{R}_{IH,cd}} \text{ for some fixed } I. \quad (2.155)$$

Finding λ

For the matrix $\mathcal{J}(\mathbf{q})$ defined in Eq. (2.155), we need to diagonalize it to find λ via the constraint in Eq.(2.128). Let $U(\mathbf{q})$ be an orthonormal diagonalizing matrix such that

$$\mathcal{J}(\mathbf{q})U(\mathbf{q}) = \mathcal{E}(\mathbf{q})U(\mathbf{q}), \quad (2.156)$$

where $\mathcal{E}(\mathbf{q}) := \text{diag}(\varepsilon_1(\mathbf{q}), \varepsilon_2(\mathbf{q}), \varepsilon_3(\mathbf{q}), \varepsilon_4(\mathbf{q}))$ and the matrices are 4×4 for the (breathing) pyrochlore lattice. Defining the cost function for a trial Lagrange multiplier λ ,

$$F(\lambda) = \frac{3}{S^2 N_s} \sum_{\mathbf{q} \in \text{BZ}} \sum_{\alpha} \frac{1}{\lambda + \beta \varepsilon_{\alpha}(\mathbf{q})} - 1, \quad (2.157)$$

then large- N requires solving for $F(\lambda) = 0$. Given system size $L \times L \times L$ unit cells, then

$$\text{BZ} = \left\{ \frac{n_1}{L} \mathbf{b}_1 + \frac{n_2}{L} \mathbf{b}_2 + \frac{n_3}{L} \mathbf{b}_3 \mid n_1, n_2, n_3 = 0, \dots, L-1 \right\} \quad (2.158)$$

are the wavevectors $\mathbf{q}$ that are summed over in the summation $\sum_{\mathbf{q} \in \text{BZ}}$. Let $\varepsilon_{\text{g.s.}} = \min_{\mathbf{q} \in \text{BZ}, \alpha} \varepsilon_{\alpha}(\mathbf{q})$ be the ground state energy, then it is convenient to shift the energy scales

as $\mathcal{J} \rightarrow \mathcal{J} - \varepsilon_{\text{g.s.}}$ to have the ground state energy at 0. With that energy shift, one can update λ to λ' such that

$$\lambda' = \lambda (F(\lambda) + 1). \quad (2.159)$$

With enough $\lambda \rightarrow \lambda'$ updates, $F(\lambda) \rightarrow 0$ should be obtained. Note that for numerical stability, it is important to keep λ positive during the iterations. When $|F(\lambda)| < \epsilon_{\text{tol}}$ for some error tolerance ϵ_{tol} (can be $\epsilon_{\text{tol}} := 10^{-8}$ for example), the iterative updates in Eq. (2.159) can be terminated and the final value of λ can be used for determining the large- N structure factor in Eq. (2.143).

Finding Specific Heat

As in the steps for finding λ , shift $\mathcal{J} \rightarrow \mathcal{J} - \varepsilon_{\text{g.s.}}$ and find λ . The large- N specific heat also depends on $\partial\lambda/\partial\beta$ and $\partial^2\lambda/\partial\beta^2$, which can be found by using Eqs.(2.147) and (2.148). Let

$$\begin{aligned} F_1 \left(\lambda, \frac{\partial\lambda}{\partial\beta} \right) &= \frac{1}{N_{\text{cell}}} \sum_{\mathbf{q} \in \text{BZ}} \sum_{\alpha} \frac{\varepsilon_{\alpha}(\mathbf{q}) + \partial\lambda/\partial\beta}{(\beta\varepsilon_{\alpha}(\mathbf{q}) + \lambda)^2}, \\ F_2 \left(\lambda, \frac{\partial\lambda}{\partial\beta}, \frac{\partial^2\lambda}{\partial\beta^2} \right) &= \frac{1}{N_{\text{cell}}} \sum_{\mathbf{q}} \sum_{\alpha} \left[\frac{\partial^2\lambda/\partial\beta^2}{(\beta\varepsilon_{\alpha}(\mathbf{q}) + \lambda)^2} - 2 \frac{(\varepsilon_{\alpha}(\mathbf{q}) + \partial\lambda/\partial\beta)^2}{(\beta\varepsilon_{\alpha}(\mathbf{q}) + \lambda)^3} \right], \end{aligned} \quad (2.160)$$

where Eq. (2.147) and Eq. (2.148) require that $F_1 \equiv 0$ and $F_2 \equiv 0$, respectively. After solving for λ , one can solve for $\partial\lambda/\partial\beta$ by fixing λ and finding $\partial\lambda/\partial\beta$ that satisfies $F_1 = 0$, and then use the values determined for λ and $\partial\lambda/\partial\beta$ as fixed values in F_2 to solve for $\partial^2\lambda/\partial\beta^2$ that satisfies $F_2 = 0$. This makes the finding of the derivatives of λ with respect to β into root-finding problems. After finding λ , $\partial\lambda/\partial\beta$ and $\partial^2\lambda/\partial\beta^2$, the specific heat can be determined by using Eq. (2.146).

2.5 Monte Carlo

Monte Carlo is a numerical probabilistic method that involves simulating system by making random updates that follow a probability distribution that fits the temperature and energy requirements. The method is named after the Monte Carlo Casino in Monaco, due to the large role that probability plays in both the Monte Carlo Casino and the numerical Monte Carlo simulations [85–88].

2.5.1 Detailed Balance

When starting from a certain system configuration, it is important to update the system in a way that is consistent with the thermodynamics. The rate of change of probability of the system being in the state $\mathcal{M}$ is

$$\frac{\partial}{\partial t}P(\mathcal{M}, t) = \sum_{\text{text } \mathcal{M}'} [w(\mathcal{M}' \rightarrow \mathcal{M})P(\mathcal{M}', t) - w(\mathcal{M} \rightarrow \mathcal{M}')P(\mathcal{M}, t)], \quad (2.161)$$

where $w(\mathcal{M} \rightarrow \mathcal{M}')$ is the probability of transition from state $\mathcal{M}$ to $\mathcal{M}'$ per unit time [11]. A sufficient condition for equilibrium is

$$P_0(\mathcal{M})w(\mathcal{M} \rightarrow \mathcal{M}') = P_0(\mathcal{M}')w(\mathcal{M}' \rightarrow \mathcal{M}). \quad (2.162)$$

Noting that the Boltzmann weights for states in thermal equilibrium are

$$P_0(\mathcal{M}) = \frac{1}{\mathcal{Z}} \exp[-\beta E(\mathcal{M})], \quad (2.163)$$

this means that systems with probability distributions that are at thermal equilibrium must satisfy the detailed balance condition:

$$\frac{w(\mathcal{M} \rightarrow \mathcal{M}')}{w(\mathcal{M}' \rightarrow \mathcal{M})} = \exp\left(-\frac{E(\mathcal{M}') - E(\mathcal{M})}{k_B T}\right). \quad (2.164)$$

A possible update method that satisfies the detailed balance condition in Eq. (2.164) is the Metropolis weight, where the transition probability per time step can be defined as

$$w(\mathcal{M} \rightarrow \mathcal{M}') = \max\left\{\exp\left(-\frac{E(\mathcal{M}') - E(\mathcal{M})}{k_B T}\right), 1\right\}. \quad (2.165)$$

Assuming each update step is 1 time unit, then the probability of an update from a state $\mathcal{M}$ to a state $\mathcal{M}'$ to take place is

$$P(\mathcal{M} \rightarrow \mathcal{M}') = \underbrace{\Delta t}_{\equiv 1} C w(\mathcal{M} \rightarrow \mathcal{M}'), \quad (2.166)$$

where C is a normalizing factor to make sure the probability of update is a valid probability (≤ 1). The Metropolis sampling is favourable when cooling down a system since it always accepts an updates that lowers the energy. In the Metropolis algorithm, using Eq. (2.166) with $C = 1$, the probability of a system in the state $\mathcal{M}$ with a proposed new state $\mathcal{M}'$ to have its proposed updated accepted is

$$P(\mathcal{M} \rightarrow \mathcal{M}') = \max\left\{\exp\left(-\frac{E(\mathcal{M}') - E(\mathcal{M})}{k_B T}\right), 1\right\}. \quad (2.167)$$

2.5.2 Over-relaxation

To improve samplings of the phase space, the over-relaxation is employed by performing local updates that do not change the energy of the configuration [87, 89]. Consider the local field at site j ,

$$\mathbf{h}_j = \frac{1}{2} \sum_k \mathcal{J}_{jk} \mathbf{S}_k. \quad (2.168)$$

with the definition in Eq. (2.168)

$$\mathcal{H} = \sum_j \mathbf{h}_j \cdot \mathbf{S}_j. \quad (2.169)$$

This means that for any spin update on site j that does not change $\mathbf{h}_j \cdot \mathbf{S}_j$, the update does not change the energy. Such an update can be done by rotating $\mathbf{S}_j$ around $\mathbf{h}_j$, as illustrated in Fig. 2.2. Recalling the Metropolis update probability used in Eq. (2.167), updates that do not change the energy have probability 1 of being accepted, meaning that the update is accepted unconditionally. To rotate a spin $\mathbf{S}_j$ around $\mathbf{h}_j$, we define the unit direction of the local field at site j

$$\hat{h} = \frac{1}{\|\mathbf{h}_j\|} \mathbf{h}_j \quad (2.170)$$

and a matrix

$$\begin{aligned} [\hat{h}]_{\times} &= \left(\underbrace{\hat{x} \times \hat{h}}_{\text{column vector}} \mid \hat{y} \times \hat{h} \mid \hat{z} \times \hat{h} \right) \\ &= \begin{pmatrix} 0 & -\hat{h}_z & \hat{h}_y \\ \hat{h}_z & 0 & -\hat{h}_x \\ -\hat{h}_y & \hat{h}_x & 0 \end{pmatrix}. \end{aligned} \quad (2.171)$$

The rotation matrix for rotating a vector around $\mathbf{h}_j$ by an angle θ is

$$\mathcal{R}_{\mathbf{h}}(\theta) = (\cos \theta) \mathbb{I} + (\sin \theta) [\hat{h}]_{\times} + (1 - \cos \theta) \underbrace{\hat{h} \hat{h}^T}_{\text{3x3 matrix}}. \quad (2.172)$$

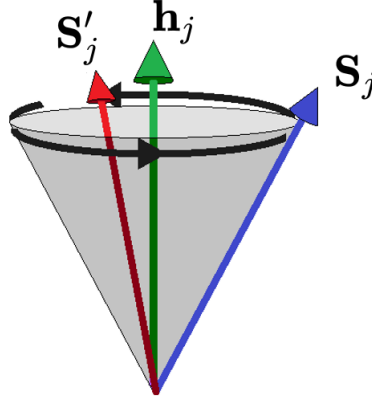


Figure 2.2: Overrelaxation of a spin in site j , with initial spin $\mathbf{S}_j$ and a local field $\mathbf{h}_j$. The spin vector is rotated around $\mathbf{h}_j$ to update the spin from $\mathbf{S}_j$ to $\mathbf{S}'_j$.

The angle of rotation, θ can be chosen randomly from $[0, 2\pi \text{ rad})$. Overrelaxation for a system of N_s spins can be done as following:

```

for  $i = 1, 2, \dots, N_s$  do
  Choose a random site  $j$ .
  Choose a random angle  $\theta \in [0, 2\pi)$ .
  Calculate local field  $\mathbf{h}_j$  using Eq. (2.168).
  Generate rotation matrix  $\mathcal{R}_{\mathbf{h}}(\theta)$  from the  $\mathbf{h}_j$ , using Eqs. (2.170)-(2.172).
  Update the spin  $\mathbf{S}_j$  to  $\mathbf{S}'_j := \mathcal{R}_{\mathbf{h}}(\theta)\mathbf{S}_j$ .
end for

```

2.5.3 Adaptive Spin Update

Ultimately, Monte Carlo involves proposing an update to the system and letting probability choose whether to accept or reject the new updated system. For simplicity, each update involves changing only one spin. With a single-spin update in mind, we would like to rotate a spin by an angle ϕ for some ϕ value that can be controlled. The direction to which the spins is rotated by ϕ , however, should be randomly chosen. For a given site j , let $\mathbf{S}_j = (s_x, s_y, s_z)$ and consider the following vectors:

$$\begin{aligned}\mathbf{v}_{\perp 1} &= \frac{1}{\sqrt{1-s_z^2}}(s_x s_z, s_y s_z, s_z^2 - 1), \\ \mathbf{v}_{\perp 2} &= \frac{1}{\sqrt{1-s_z^2}}(-s_y, s_x, 0).\end{aligned}\tag{2.173}$$

If $s_z \approx 0$, $\mathbf{v}_{\perp 1}$ and $\mathbf{v}_{\perp 2}$ can be defined replacing the z -component with the x or y -component in Eq. (2.173). $\{\mathbf{S}_j, \mathbf{v}_{\perp 1}, \mathbf{v}_{\perp 2}\}$ are all mutually orthogonal. To rotate $\mathbf{S}_j$, we need to choose an axis of rotation that is randomly-chosen and ideally orthogonal to $\mathbf{S}_j$. A rotation axis that satisfies these criteria can be defined as

$$\mathbf{u} = (\cos \theta) \mathbf{v}_{\perp 1} + (\sin \theta) \mathbf{v}_{\perp 2},\tag{2.174}$$

where $\theta \in [0, 2\pi \text{ rad})$ is a randomly chosen angle. With an axis of rotation chosen, one can rotate $\mathbf{S}_j$ around $\mathbf{u}$ by an angle ϕ that is adjusted to ensure an acceptance rate of 50% if possible. To do that, one can track some number N_{prop} of proposed spin updates, and N_{acc} , number of spin updates that were accepted out of the most recent N_{prop} propositions, to update the angle of rotation ϕ as

$$\phi \rightarrow \phi \times \frac{2N_{\text{acc}}}{N_{\text{prop}}}.\tag{2.175}$$

As long as N_{prop} is large enough to have a representative sample of accepted and rejected spin updates, one should expect this update to lead to the optimal $N_{\text{acc}}/N_{\text{prop}} \approx 0.5$. Illustrations of rotating a spin by a set angle ϕ in a random direction is shown in Fig.(2.3).

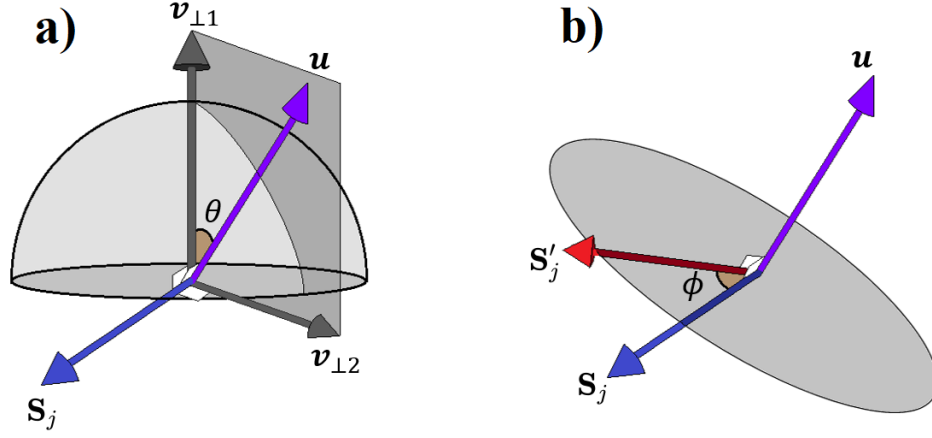


Figure 2.3: Schematic of rotating a spin vector $\mathbf{S}_j$ into a new vector $\mathbf{S}'_j$. **a)** A random unit vector $\mathbf{u}$ is chosen in the plane orthogonal to $\mathbf{S}_j$. **b)** An spin update by rotating $\mathbf{S}_j$ around $\mathbf{u}$ to make the spin at site j be $\mathbf{S}'_j$.

For a system with N_s spins, it is convenient to group a sequence of N_s randomly chosen spin updates into a single “sweep”. The algorithm for a Monte Carlo sweep is as follows:

```

for  $i = 1, 2, \dots, N_s$  do
  Choose a random site  $j$ , which has spin  $\mathbf{S}_j$ .
  For a randomly chosen  $\theta$  to obtain  $\mathbf{u}$  unit vector from Eq. (2.174).
  Rotate  $\mathbf{S}_j$  around  $\mathbf{u}$  by an angle  $\phi$  to get new spin  $\mathbf{S}'_j$ .
  Calculate the local field  $\mathbf{h}_j$  as done in Eq. ((2.168)).
  Calculate the energy cost of the update,  $\Delta E = \mathbf{h}_j \cdot (\mathbf{S}'_j - \mathbf{S}_j)$ .
  Generate a random  $\alpha \in [0, 1)$ 
  if  $\alpha \leq e^{-\Delta E/T}$  for temperature  $T$  then
    set  $\mathbf{S}_j \leftarrow \mathbf{S}'_j$ 
  end if
end for

```

2.5.4 Extracting Data

In a Monte Carlo simulations, the values of system variables such as spins and energy fluctuate even when the system is thermalized. For this reason, it is important to sample

the system's configurations over multiple system updates. Moreover, when averaging over multiple configurations, it is important for the configurations' correlations with each other to be negligible. This means that samplings of the system's configurations should be spread apart in time enough for the sampled microstates to be significantly different from each other. This requires samplings to be spread apart by a sufficient number of Monte Carlo updates (sweeps and overrelaxations), although the necessary number of such updates depends on the system. When the system's temperature changes, it is also important to let the system undergo enough updates to reach its new thermal equilibrium (thermalize). The minimum number of sweeps that are needed for the system to thermalize properly depend on the system.

Structure Factor

Consider a three-dimensional lattice with $L \times L \times L$ unit cells. The lattice has primitive translation vectors $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$, and reciprocal lattice vectors $\mathbf{b}_1$, $\mathbf{b}_2$, $\mathbf{b}_3$. From Eqs. (2.11) and (2.20), the structure factor for models with isotropic spin Hamiltonians (such as Heisenberg) can be written as

$$S(\mathbf{q}) = \langle \mathbf{s}(\mathbf{q}) \cdot \mathbf{s}(-\mathbf{q}) \rangle = \langle |\mathbf{s}(\mathbf{q})|^2 \rangle, \quad (2.176)$$

and

$$\mathbf{s}(\mathbf{q}) = \sum_c \mathbf{s}_c(\mathbf{q}), \quad (2.177)$$

where c is the sublattice index, and $\mathbf{s}_c(\mathbf{q})$ is defined as

$$\mathbf{s}_c(\mathbf{q}) = e^{-i\mathbf{q} \cdot \mathbf{r}_c} \sum_I \mathbf{S}_{I,c} e^{-i\mathbf{q} \cdot \mathbf{R}_I}. \quad (2.178)$$

For a system with $L \times L \times L$ unit cells, the unit cells index I can be defined as

$$I = (n_1, n_2, n_3), \quad n_1, n_2, n_3 \in \{0, 1, \dots, L-1\}. \quad (2.179)$$

The position for unit cell with index n_1, n_2, n_3 is then

$$\mathbf{R}_{n_1 n_2 n_3} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3, \quad n_1, n_2, n_3 \in \{0, 1, \dots, L-1\}. \quad (2.180)$$

The wavevectors in the system are also constrained, with a Brillouin zone defined as

$$\mathbf{q} = \frac{m_1}{L}\mathbf{b}_1 + \frac{m_2}{L}\mathbf{b}_2 + \frac{m_3}{L}\mathbf{b}_3, \quad m_1, m_2, m_3 \in \{0, 1, \dots, L-1\}. \quad (2.181)$$

Let

$$\mathbf{S}_{n_1 n_2 n_3, c} = \mathbf{S}(\mathbf{R} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3 + \mathbf{r}_c) \quad (2.182)$$

be the spin at unit cell index (n_1, n_2, n_3) and sublattice index c . Let

$$\hat{\mathbf{s}}_{m_1 m_2 m_3, c} = \mathbf{s}_c \left(\mathbf{q} = \frac{m_1}{L}\mathbf{b}_1 + \frac{m_2}{L}\mathbf{b}_2 + \frac{m_3}{L}\mathbf{b}_3 \right) \quad (2.183)$$

be the Fourier-transform of the spins at sublattice index c , as defined in Eq. (2.178). Let

$$S(m_1, m_2, m_3) = S \left(\mathbf{q} = \frac{m_1}{L}\mathbf{b}_1 + \frac{m_2}{L}\mathbf{b}_2 + \frac{m_3}{L}\mathbf{b}_3 \right) \quad (2.184)$$

be the structure factor at the defined $\mathbf{q}$ value. The discrete representations of the structure factor as a function of wavevector indices (m_1, m_2, m_3) is useful for representing the Fourier transforms of the spins in the lattice. Using Eqs. (2.177) in (2.183), we get

$$\hat{\mathbf{s}}_{m_1 m_2 m_3, c} = e^{-i\mathbf{r}_c \cdot \left(\frac{m_1}{L}\mathbf{b}_1 + \frac{m_2}{L}\mathbf{b}_2 + \frac{m_3}{L}\mathbf{b}_3 \right)} \sum_{n_1, n_2, n_3=0}^{L-1} \mathbf{S}_{n_1 n_2 n_3, c} e^{-i\frac{2\pi}{L}(n_1 m_1 + n_2 m_2 + n_3 m_3)}. \quad (2.185)$$

The structure factor can then be obtained from plugging Eqs. (2.176) and (2.177) into Eq. (2.184) to get

$$S(m_1, m_2, m_3) = \langle \left| \sum_c \hat{\mathbf{s}}_{m_1 m_2 m_3, c} \right|^2 \rangle, \quad (2.186)$$

for $\hat{\mathbf{s}}_{m_1 m_2 m_3, c}$ given in Eq. (2.185).

Specific Heat and Susceptibility

To extract the specific heat of the system, it is useful to sample the energy, $E = \mathcal{H}(\mathcal{M})$, and the square-energy, E^2 of the system between Monte Carlo update. By taking the average of these sampled quantities over multiple configurations, $\langle E \rangle$ and $\langle E^2 \rangle$ can be used in Eq. (2.27), to obtain the specific heat of the system. The uniform-field susceptibility can be obtained likewise by sampling the magnetization $M = \left\| \sum_{j=1}^{N_s} \mathbf{S}_j \right\|$ and M^2 and using their averages in Eq. (2.35).

2.6 Chapter Summary

In this chapter, we went over methods to extract information on the neutron scattering differential cross section, specific heat, and susceptibility from theoretical analysis methods of the model used to describe $\text{CuAlCr}_4\text{S}_8$. We also went through the theory behind MFT, large- N , and Monte Carlo simulations. The results from the analytic MFT and large- N methods are presented in Chapter 3, while the results from the numerical Monte Carlo method are presented in Chapter 4.

Chapter 3

Semi-Analytical Results

As previously established in Section 1.3, the theoretical models treat $\text{CuAlCr}_4\text{S}_8$ as a Heisenberg model on a breathing pyrochlore lattice. Initially, the model used was Heisenberg with exchange couplings up to third-nearest neighbours, obtained by our collaborators using density-functional theory (DFT). One set goes up to J_{3b} couplings, and a more recent set of parameters goes up to fifth-nearest neighbour couplings J_5 , with the displacements corresponding to the couplings shown in Fig. 3.1. These “up-to-3rd NN” and the “up-to-5th NN” sets of parameters are given in Table 3.1. Since the geometric breathing ratio for $\text{CuAlCr}_4\text{S}_8$ is close to 1 (the “large” tetrahedra are only $\approx 7\%$ longer than the “small” tetrahedra), and because setting the geometric breathing ratio to be exactly 1 does not affect the qualitative results in all the methods tested, all the original data and our collaborators’ theoretical data assumes that the geometric breathing ratio of the breathing pyrochlore is 1. With that assumption, the pyrochlore is still a breathing pyrochlore due to the breaking of inversion symmetry, since the model is differentiating between $1a$ nearest neighbours and $1b$ nearest neighbours.

The Hamiltonian in the up-to-3rd-NN model can be rewritten explicitly from Eq. (2.54) as

$$\begin{aligned} \mathcal{H} = & \frac{J_{1a}}{2} \sum_{j' \in \mathcal{N}_j^{(1a)}} \mathbf{s}_j \cdot \mathbf{s}_{j'} + \frac{J_{1b}}{2} \sum_{j' \in \mathcal{N}_j^{(1b)}} \mathbf{s}_j \cdot \mathbf{s}_{j'} + \frac{J_2}{2} \sum_{j' \in \mathcal{N}_j^{(2)}} \mathbf{s}_j \cdot \mathbf{s}_{j'} \\ & + \frac{J_{3a}}{2} \sum_{j' \in \mathcal{N}_j^{(3a)}} \mathbf{s}_j \cdot \mathbf{s}_{j'} + \frac{J_{3b}}{2} \sum_{j' \in \mathcal{N}_j^{(3b)}} \mathbf{s}_j \cdot \mathbf{s}_{j'}, \end{aligned} \quad (3.1)$$

where $j' \in \mathcal{N}_j^{(k)}$ stands for “ j' and j are k^{th} -nearest neighbours”, the divisions by 2 are there

to account for double counting, and the J_k coefficients are given from the up-to-3rd-NN row in Table 3.1.

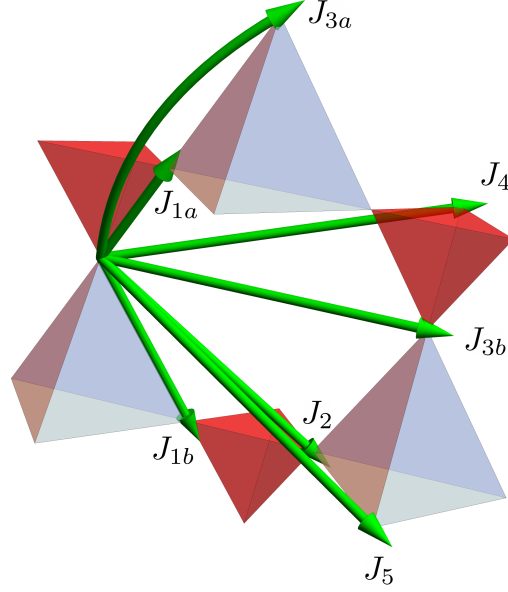


Figure 3.1: In the model, the magnetic Cr^{3+} ions are the spins, located at the corners of the tetrahedra. Exact coordinates corresponding to the displacement between each type of neighbours is provided in Appendix A.

Model	J_{1a} (K)	J_{1b} (K)	J_2 (K)	J_{3a} (K)	J_{3b} (K)	J_4 (K)	J_5 (K)
up-to-3 rd -NN	-0.2(2)	-2.7(2)	0.1(1)	6.0(1)	3.5(1)	0	0
up-to-5 th -NN	2.0(5)	-4.6(5)	1.1(3)	5.9(2)	3.3(2)	-1.0(2)	0.2(2)

Table 3.1: Table of exchange couplings used in the Heisenberg model for $\text{CuAlCr}_4\text{S}_8$.

The Hamiltonian in the up-to-5th-NN model can be rewritten explicitly from Eq. (2.54) as

$$\begin{aligned}
\mathcal{H} = & \frac{J_{1a}}{2} \sum_{j' \in \mathcal{N}_j^{(1a)}} \mathbf{s}_j \cdot \mathbf{s}_{j'} + \frac{J_{1b}}{2} \sum_{j' \in \mathcal{N}_j^{(1b)}} \mathbf{s}_j \cdot \mathbf{s}_{j'} + \frac{J_2}{2} \sum_{j' \in \mathcal{N}_j^{(2)}} \mathbf{s}_j \cdot \mathbf{s}_{j'} \\
& + \frac{J_{3a}}{2} \sum_{j' \in \mathcal{N}_j^{(3a)}} \mathbf{s}_j \cdot \mathbf{s}_{j'} + \frac{J_{3b}}{2} \sum_{j' \in \mathcal{N}_j^{(3b)}} \mathbf{s}_j \cdot \mathbf{s}_{j'} \\
& + \frac{J_4}{2} \sum_{j' \in \mathcal{N}_j^{(4)}} \mathbf{s}_j \cdot \mathbf{s}_{j'} + \frac{J_5}{2} \sum_{j' \in \mathcal{N}_j^{(5)}} \mathbf{s}_j \cdot \mathbf{s}_{j'}, \tag{3.2}
\end{aligned}$$

where the J_k coefficients are given from the “up-to-5th-NN” row in Table 3.1, and this means that they are different from the J_k coefficients in Eq. (3.1). We investigate the results predicted for both sets of coupling to assess any changes between the models. Besides those two sets of parameters, the systems were investigated using large- N for sets of parameters that are slight alterations of the two existing parameter sets. The intention of investigating the system with altered exchange parameters is to examine the sensitivity of the results to perturbations in the Hamiltonian. The up-to-3rd-NN parameter set is sensitive to perturbations since the ordering wavevectors change under slight perturbations. The sensitivity on the ordering wavevector for the up-to-3rd-NN parameters may be related to the degeneracy of the ground-state manifold, which is prone to being broken under small perturbations.

3.1 Energy Bands

The exchange coupling matrix in momentum space, $\mathcal{J}(\mathbf{q})$, defined in Eq. (2.59), has eigenvalues that corresponds to the energy bands at each wavevector $\mathbf{q}$. The up-to-3rd-NN couplings result in the ordering wavevectors forming degeneracy lines of the form $\mathbf{q} = \pi/a(2, k, 0)$, as can be seen in the flat segment of the bottom band in Fig. 3.2. On the other hand, the up-to-5th-NN coupling do not have the degeneracy line in the lower band, but instead the energy is minimized for wavevectors of the form $\pi/a(2, 0, 0)$ and $\pi/a(2, 2, 0)$, as can be seen by the minimum in the lowest band in Fig. 3.3.

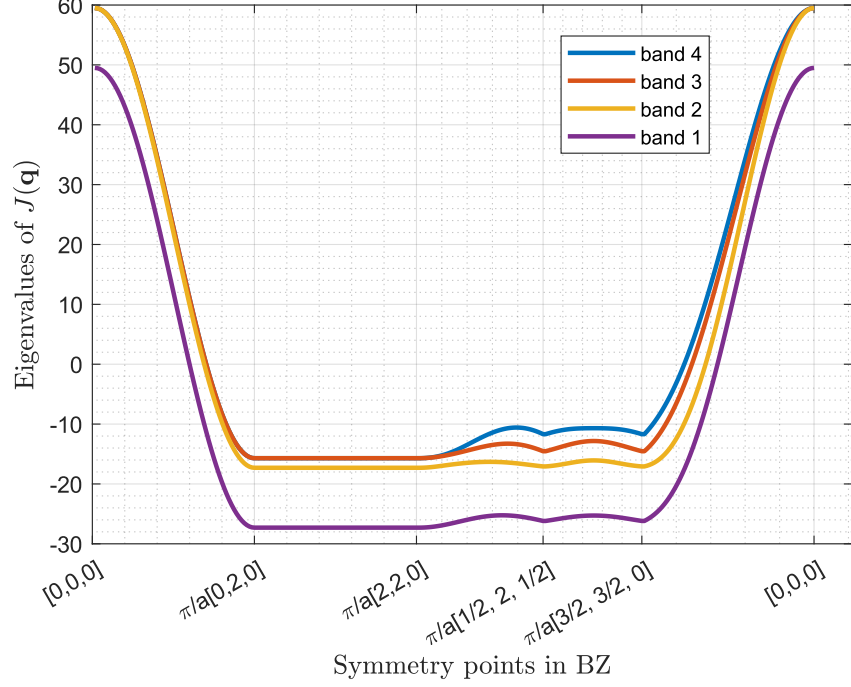


Figure 3.2: Exchange coupling eigenvalue bands for a selected path in the Brillouin zone, for the up-to-3rd-NN model. The eigenvalues are of the Fourier-transformed exchange coupling matrix, $\mathcal{J}(\mathbf{q})$, defined in Eq. (2.59). Note that the absolute minimum of the lowest eigenvalue is attained along a degeneracy line passing through $\frac{\pi}{a}[0, 2, 0]$ and $\frac{\pi}{a}[2, 2, 0]$. The degeneracy line means that internal energy does not select a single well-defined ordering wavevector, although other phenomena such as ObD may narrow down the set of ordering wavevectors. Since the minima are not at $\mathbf{q} = 0$, this suggests that the ordering of the spin cannot be represented by a single unit cell, since the wavelength of the ordering wavevectors spans multiple unit cells.

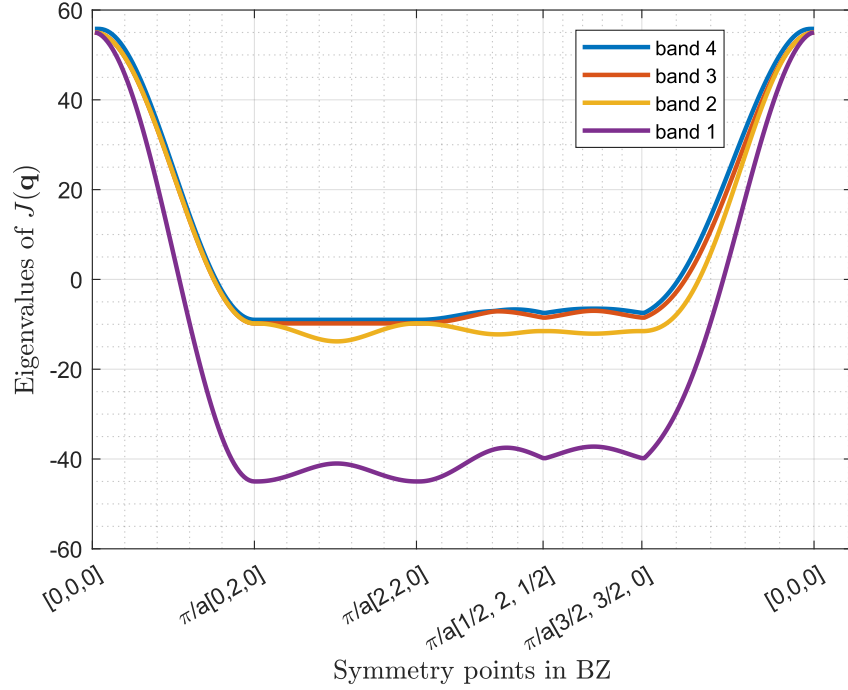


Figure 3.3: Exchange coupling eigenvalue bands for a selected path in the Brillouin zone, for the up-to-5th-NN model. The minima at the lowest band for wavevectors $\pi/a[0, 2, 0]$ and $\pi/a[2, 2, 0]$ are global minima and thus the classical ordering wavevectors.

3.2 Mean Field Theory

3.2.1 Critical Temperature

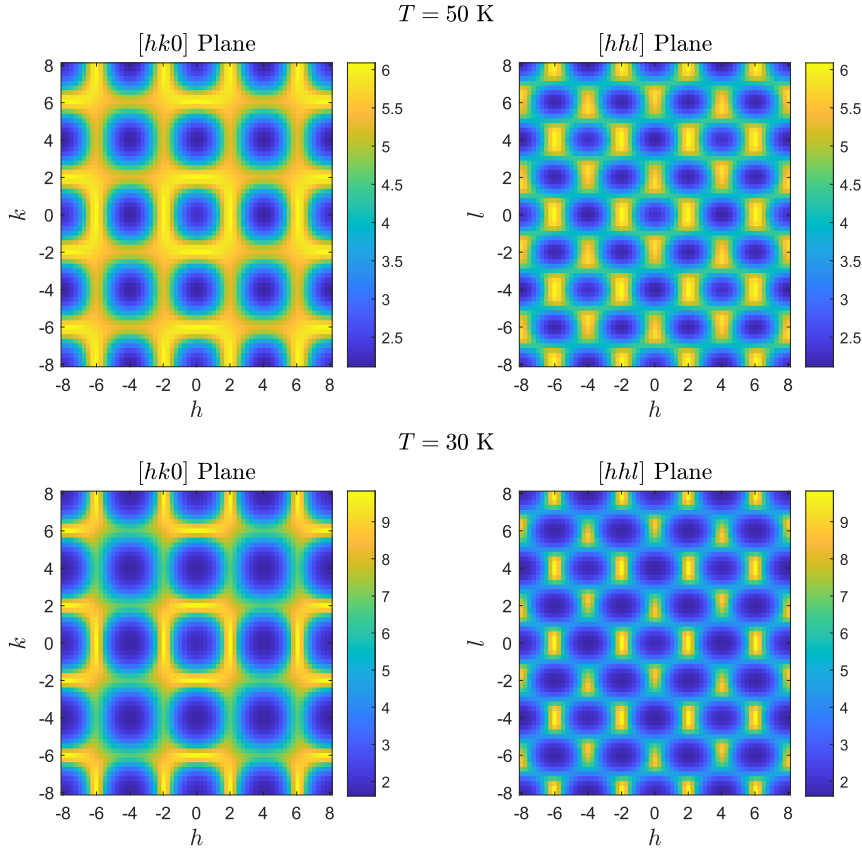
Using (2.111), the up-to-3rd-NN and up-to-5th-NN models have mean-field critical temperatures of 20.475 K and 33.75 K, respectively. For comparison, the experimental value for the critical temperature is about 20 K [33]. Although this suggests that the up-to-3rd-NN agrees more with experiment, the mean-field critical temperature is not as reliable as the critical temperatures obtained from numerical methods such as Monte Carlo, since the mean-field approximations is ingrained with assumptions that are only valid when well above the critical temperature. The critical temperatures from Monte Carlo are given in Chapter 4.

3.2.2 Structure Factor

The MFT structure factor is obtained using Eq. (2.113).

Up to 3rd Nearest Neighbours

Temperatures lower than T_C^{MF} give negative values for the structure factor, which is non-physical. We will see in Chapter 4 that the more accurate Monte Carlo simulation has a critical temperature that is about half of T_C^{MF} . For these reason, mean-field theory is subject to scrutiny when it comes to predicting temperatures of phase transitions. As seen in Fig. 3.4, the structure factor peaks form box patterns in the $[hk0]$ plane. When nearing T_C^{MF} from above, the box pattern, which is on the degeneracy line of ordering wavevectors, has a modulation of the structure factor that peaks at the midpoint of the box edges $2\pi/a(1, 0, 0)$. However, the peak does not approach a point-wise singularity.



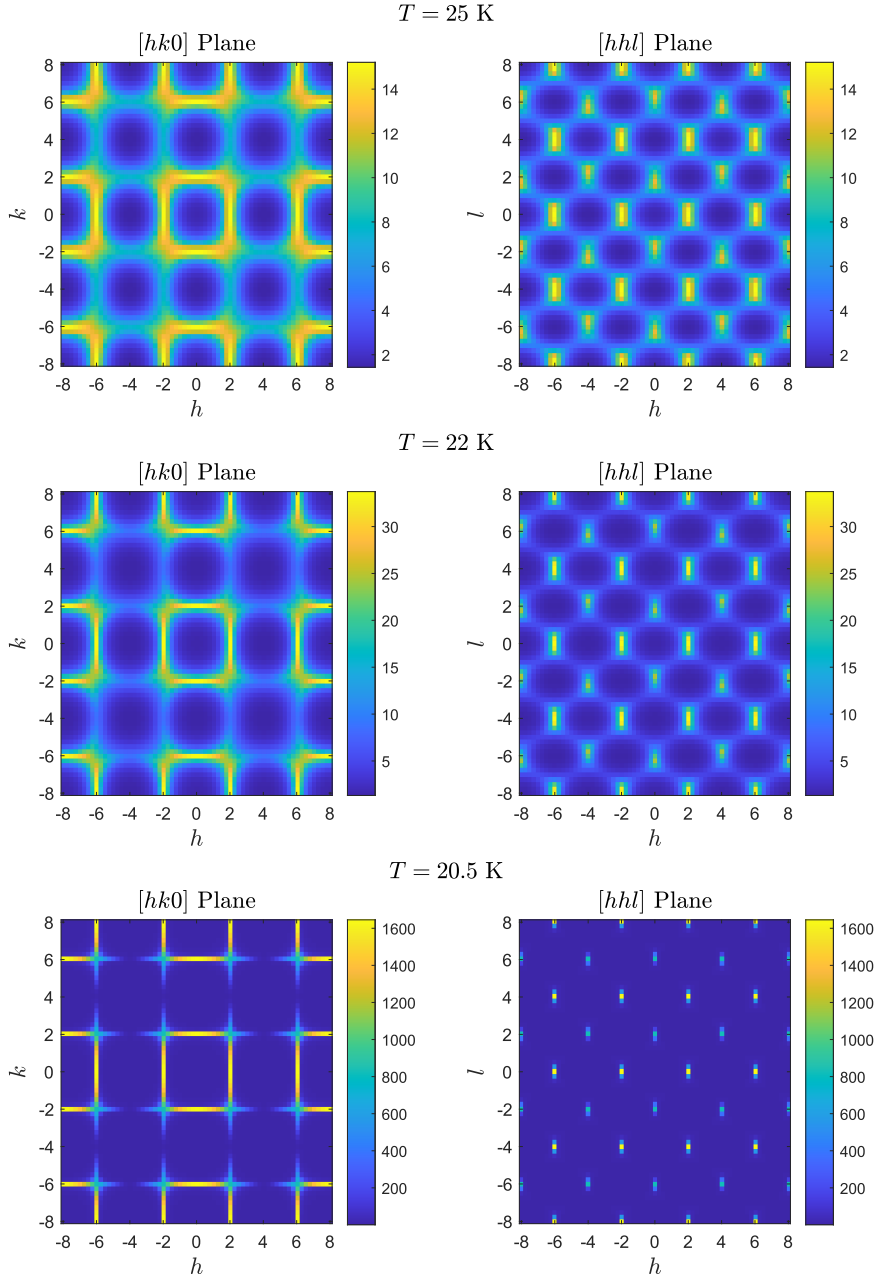
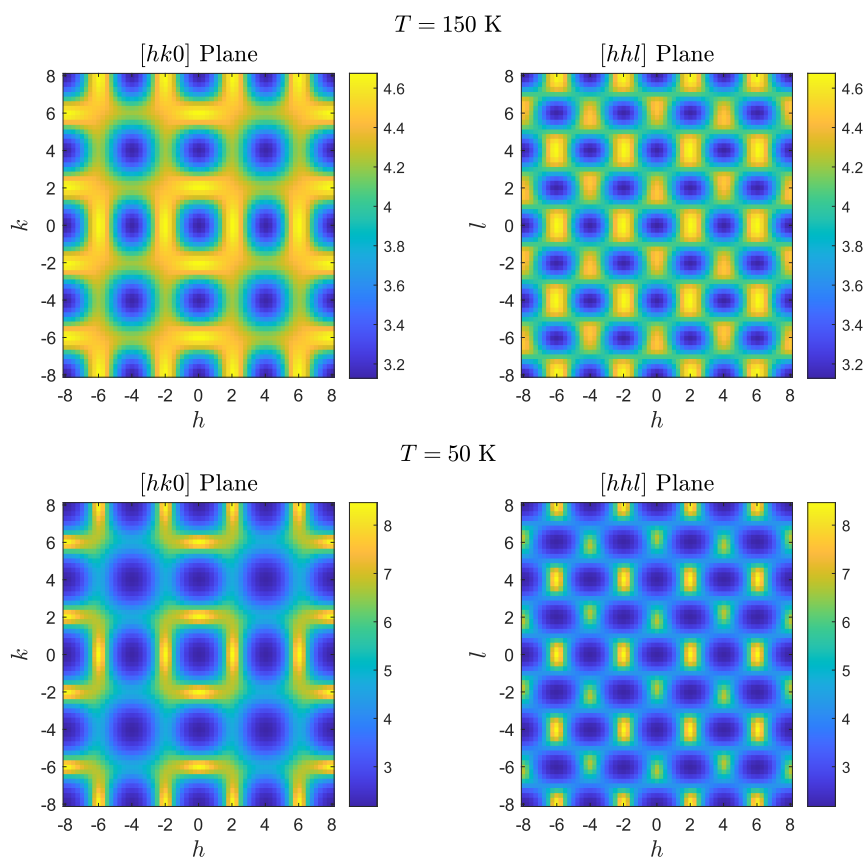


Figure 3.4: Plots of MFT structure factor for $\text{CuAlCr}_4\text{S}_8$ model up to J_{3b} , spin modulus $S = 3/2$, the MFT critical temperature is $T_C^{\text{MF}} = 20.475 \text{ K}$.

While the structure factors presented in Fig. 3.4 show the highest structure factor intensities along the degeneracy ground-state lines, the structure factor varies along the degeneracy lines. When compared with the AFM nearest-neighbour model on the FCC lattice, which has the same set of ordering wavevectors forming degeneracy lines, the MFT structure factor for the AFM nearest-neighbour model on the FCC lattice give a constant intensity in the structure factor along the degeneracy lines (as shown in Fig. B.3 in Appendix B.2). The variation of the structure factor along the degeneracy lines in the up-to-3rd-NN model is due to the tetrahedral unit cells in the breathing pyrochlore having a wavevector-dependent form factor that affects the structure factor. Due to interference between wavevectors and the tetrahedral unit cells, the form factors maximize the MFT structure factors at the mid-points of the box edges, as seen in Figs. 3.4.

Up to 5th Nearest Neighbours

Like the up-to-3rd-NN model, the structure factor for the up-to-5th-NN model gives unphysical negative values for structure factor at temperatures lower than the model's respective critical temperature (33.75 K). At high temperatures, the structure factor peaks at the same box pattern as the up-to-3rd-NN model. A crucial difference is in the low temperature regime, where discrete intensity peaks form at the ordering wavevectors, which form at the midpoint of the box edges ($2\pi/a(1, 0, 0)$) and the box corners ($2\pi/a(1, 1, 0)$). The peaks at the midpoint of the box edges are more intense than the one at the box corners, but both peaks in the structure factor approach a singularity as the temperature approaches $T_C^{\text{MF}} = 33.75$ K from above.



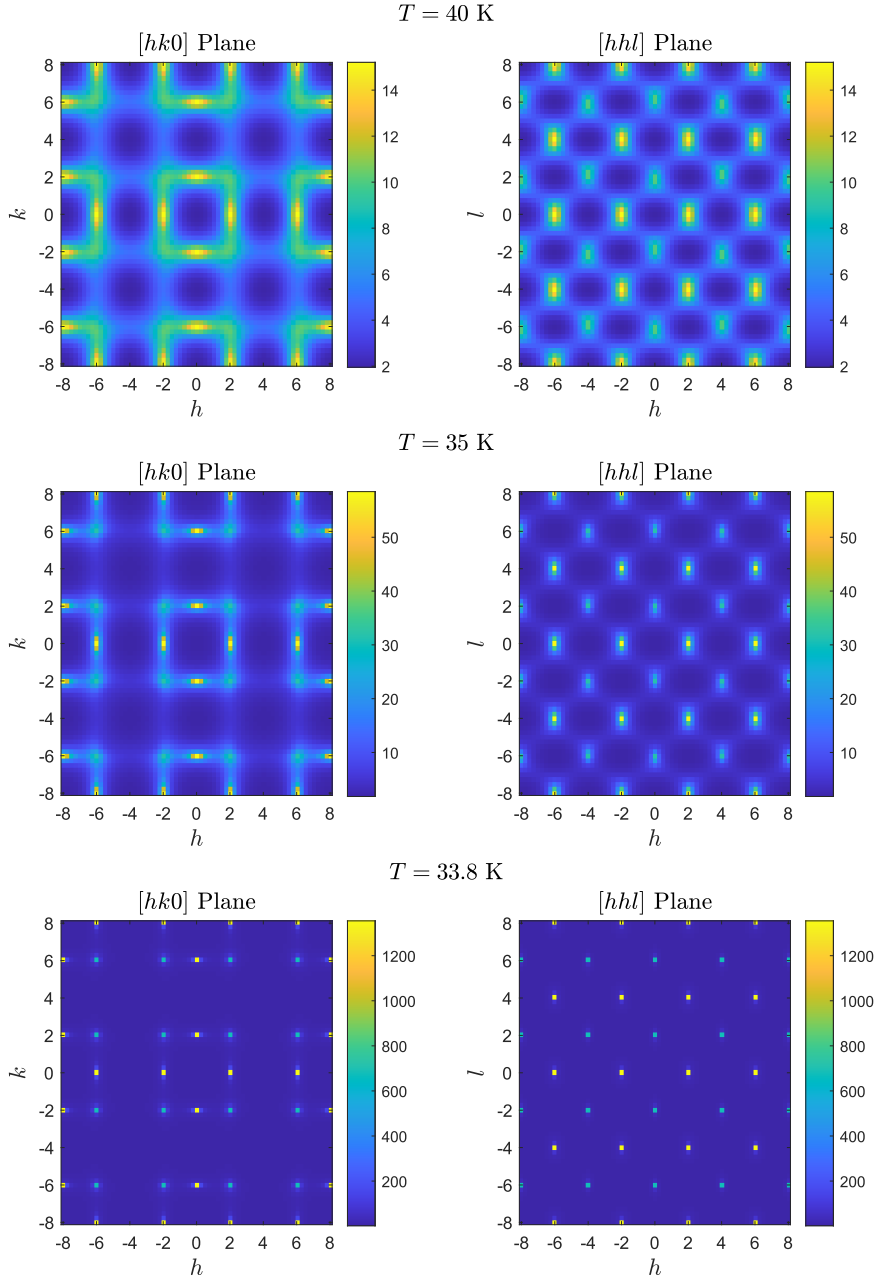


Figure 3.5: Plots of MFT structure factor for the $\text{CuAlCr}_4\text{S}_8$ model up to J_5 , spin modulus $S = 3/2$. The MFT critical temperature is $T_C^{\text{MF}} = 33.75 \text{ K}$.

3.3 Large- N

Unlike MFT, large- N has a constraint that satisfies the average norm of the spin. While large- N gives well-defined numerical values for any nonzero temperature, while MFT which is restricted to $T > T_C^{\text{MF}}$. However, the large- N fails to capture a phase transition, in the sense that the heat capacity does not form a peak that sharpens about the critical temperature as the system size is increased. This disagrees with experimental data for $\text{CuAlCr}_4\text{S}_8$, where a magnetic phase transition was observed [33]. While no clear phase transition was observed from large- N for both the up-to-3rd-NN and the up-to-5th-NN models, we will see in Chapter 4 that classical Monte Carlo simulations do display a phase transition.

3.3.1 Specific Heat and Susceptibility

Up to 3rd Nearest Neighbours

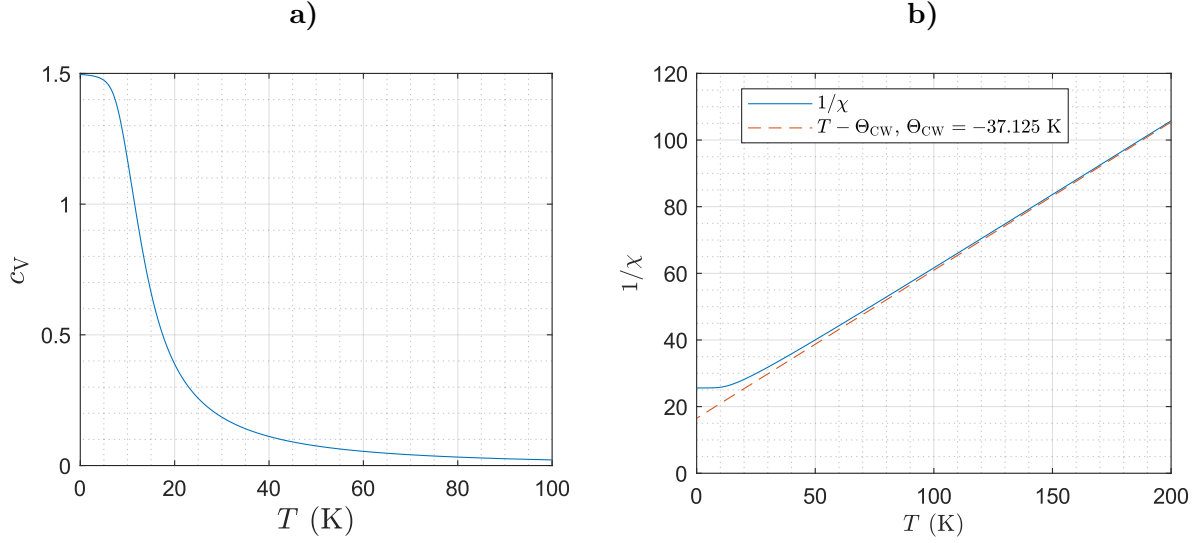


Figure 3.6: Large- N analysis for model with exchange couplings up to 3rd NN. **a)** Specific heat versus temperature. There is no sign of a phase transition since the heat capacity remains continuous, but the curve does flatten at around $T \approx 10$ K. The absence of a singularity in the heat capacity is due to approximations made in large- N . Large- N also fails to capture a singularity in the specific heat for the ferromagnetic nearest-neighbour simple cubic Heisenberg model (for which there should be a phase transition with an infinite heat capacity [2]). **b)** Reciprocal susceptibility, with asymptote to the Curie-Weiss temperature, given by Eq. (2.40). The high temperature behaviour agrees with the Curie-Weiss law.

Up to 5th Nearest Neighbours

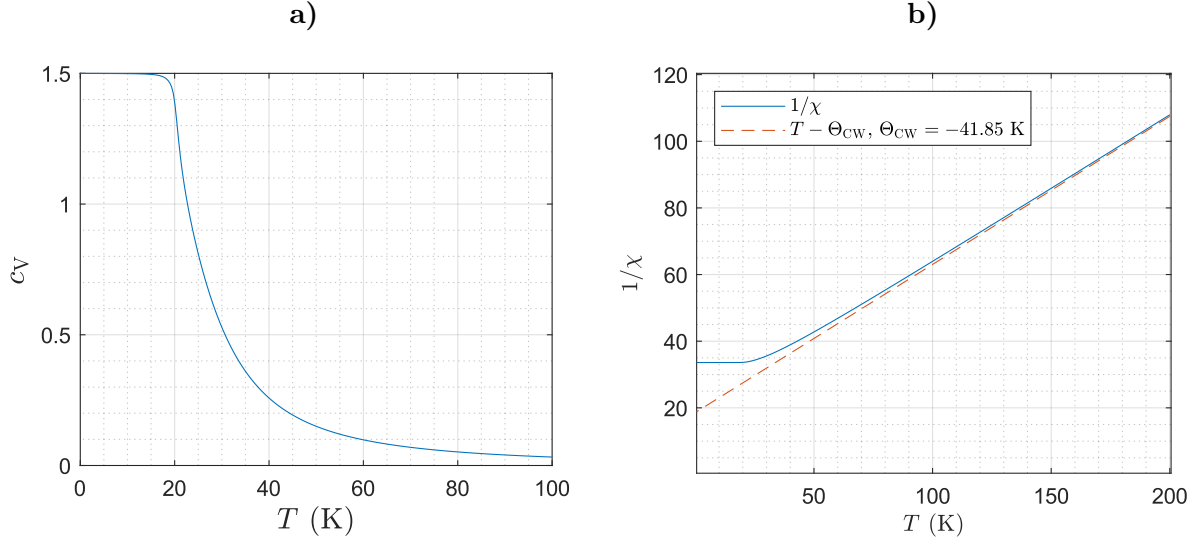


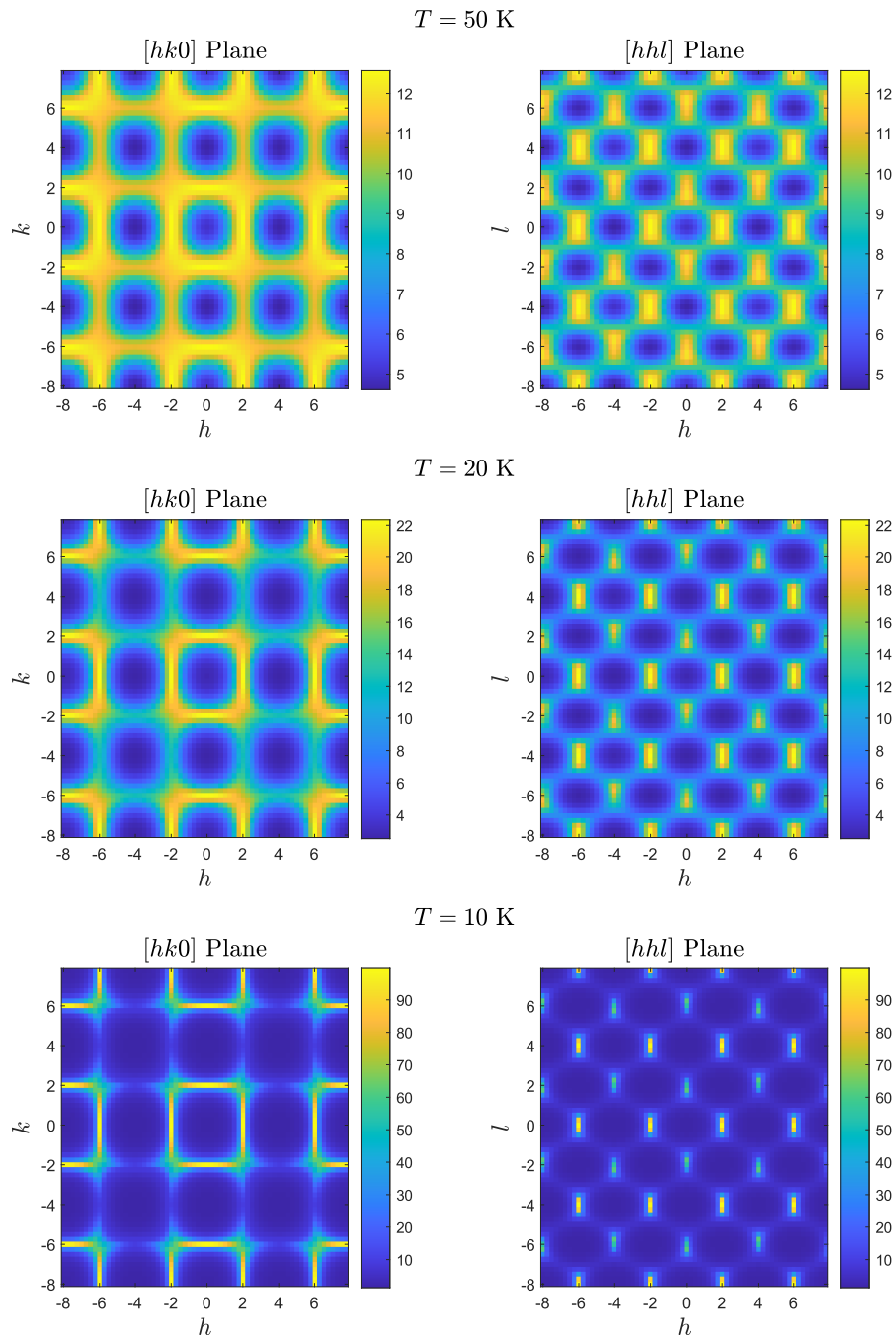
Figure 3.7: Large- N analysis for model with exchange couplings up to J_5 **a)** Specific heat. Like Fig. 3.6a), there is no indication of a phase transition in the heat capacity, but a flattening of the curve below a certain temperature. For the up-to-5th-NN parameters, this flattening takes place at around ≈ 20 K. **b)** Reciprocal susceptibility, with asymptote to the Curie-Weiss temperature, which is -41.85 K for the specific exchange couplings in the model.

3.3.2 Structure Factor

Like mean-field theory, a notable feature of the structure factor is the intensity peak in the $[hk0]$ plane along a box with corners at $\frac{2\pi}{a}(\pm 1, \pm 1, 0)$.

Up to 3rd Nearest Neighbours

Plots of the large- N structure factor for up-to-3rd-NN model are shown in Fig. 3.8.



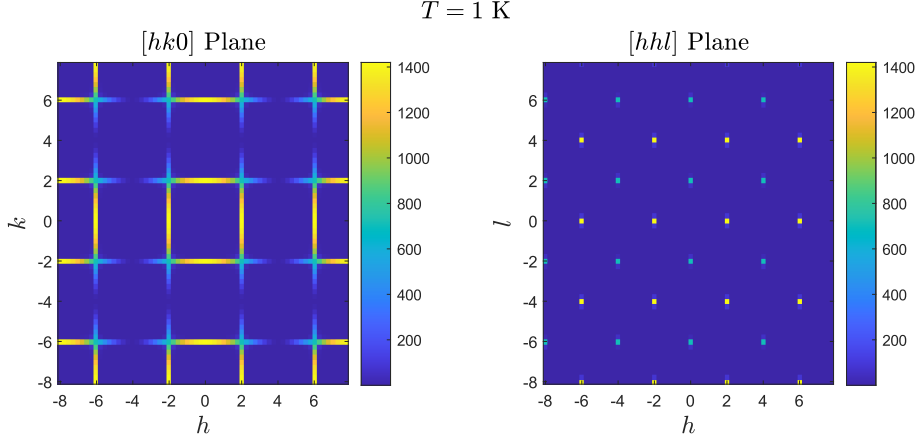


Figure 3.8: Plots of large- N structure factor with up-to-3rd-NN exchange coupling at various temperatures.

Like the results from MFT for the up-to-3rd-NN model (given in Fig. 3.4), the structure factor for large- N in Fig. 3.8 has lines of high intensities along the degeneracy lines. Like MFT, the structure factor is not uniform along the degeneracy lines due to the tetrahedral unit cells' form factor.

The powder average, seen at Fig. 3.9 and obtained by using Eq. (2.47), suggests peaks at $\|\mathbf{Q}\| = \frac{2\pi}{a}, \frac{6\pi}{a}, \frac{10\pi}{a} \approx 0.63 \text{ \AA}, 1.89 \text{ \AA}, 3.15 \text{ \AA}$, which are all commensurate with the size of the Brillouin zone. These peaks sharpen as the temperature decrease, but the peaks maintain some width rather than becoming infinitesimally narrow. The peaks' residual width at low temperatures is expected since the high-intensity points in the structure factor are not discrete points, but rather a continuous set that spans across a range of wavevectors (specifically the ordering wavevectors on the ground state degeneracy lines). The peaks' growth is continuous with temperature rather than being an abrupt appearance, since large- N for the up-to-3rd-NN model displays the ordering at low temperatures as a continuous process rather than an abrupt phase transition. In Chapter 4, we will see that like large- N , Monte Carlo simulations give structure factor peaks at the midpoints of the box edges, $\mathbf{q} = 2\pi/a(1, 0, 0)$. Moreover, Monte Carlo simulations give peaks at the corners of the box, $\mathbf{q} = 2\pi/a(1, 1, 0)$. These peaks would also be expected to repeat in momentum space according to reciprocal lattice translations, which have the form $\mathbf{G} = 2\pi/a(q, r, s)$ for integers q, r, s such that $q + r + s$ is even. For these reasons, we expect the powder average to have peaks at the moduli of wavevectors of the form $\frac{\pi}{a}(2h, 2k, 2l)$, which are $\frac{2\pi}{a}\sqrt{n}$ for some integer n . These wavevector moduli are marked in Fig. 3.9 as red vertical dashed lines. However, the peaks in the plots in Fig. 3.9 at $\|\mathbf{Q}\| = 2\pi/a, 6\pi/a, 10\pi/a \approx 0.63 \text{ \AA}$,

1.89 Å, 3.15 Å all correspond to reciprocal lattice translations of $\mathbf{q} = 2\pi/a(1, 0, 0)$, while there are no peaks corresponding to the ones we shall see in Chapter 4 from Monte Carlo simulations, $\mathbf{q} = 2\pi/a(1, 1, 0)$.

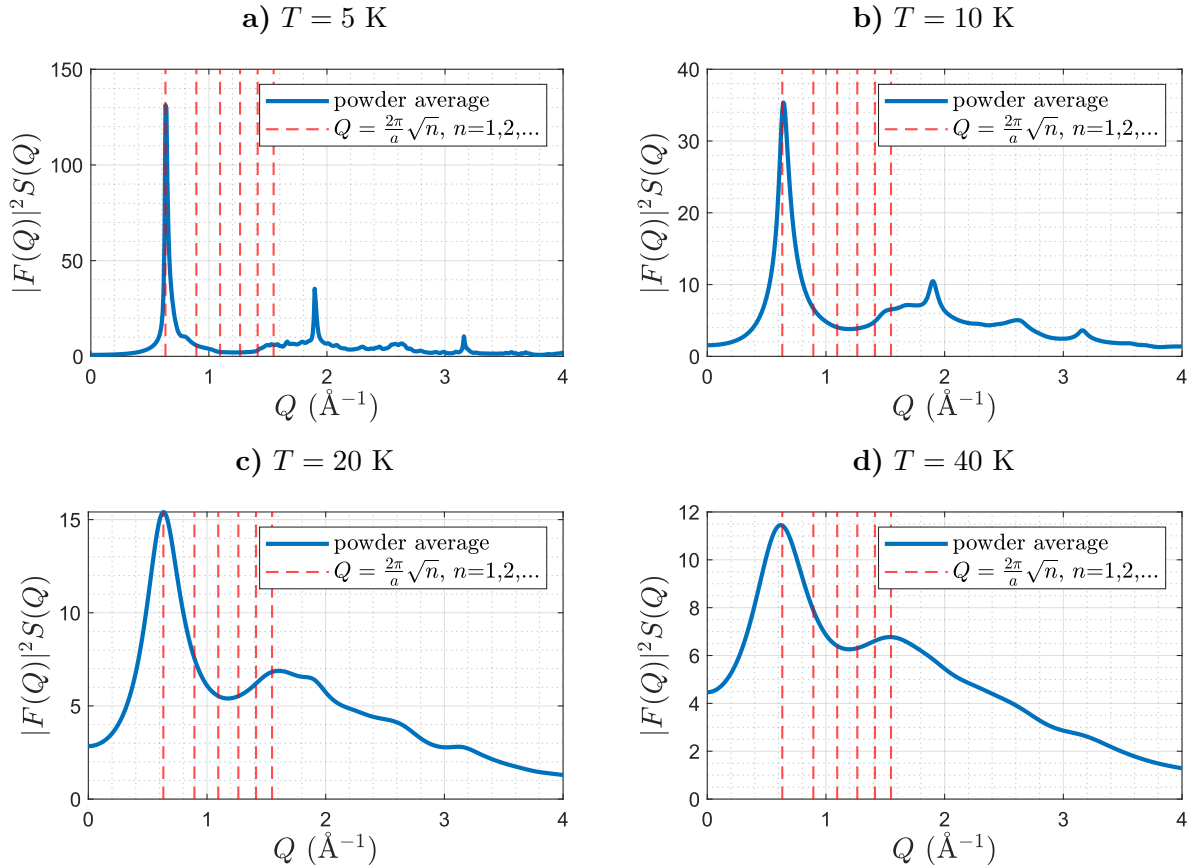
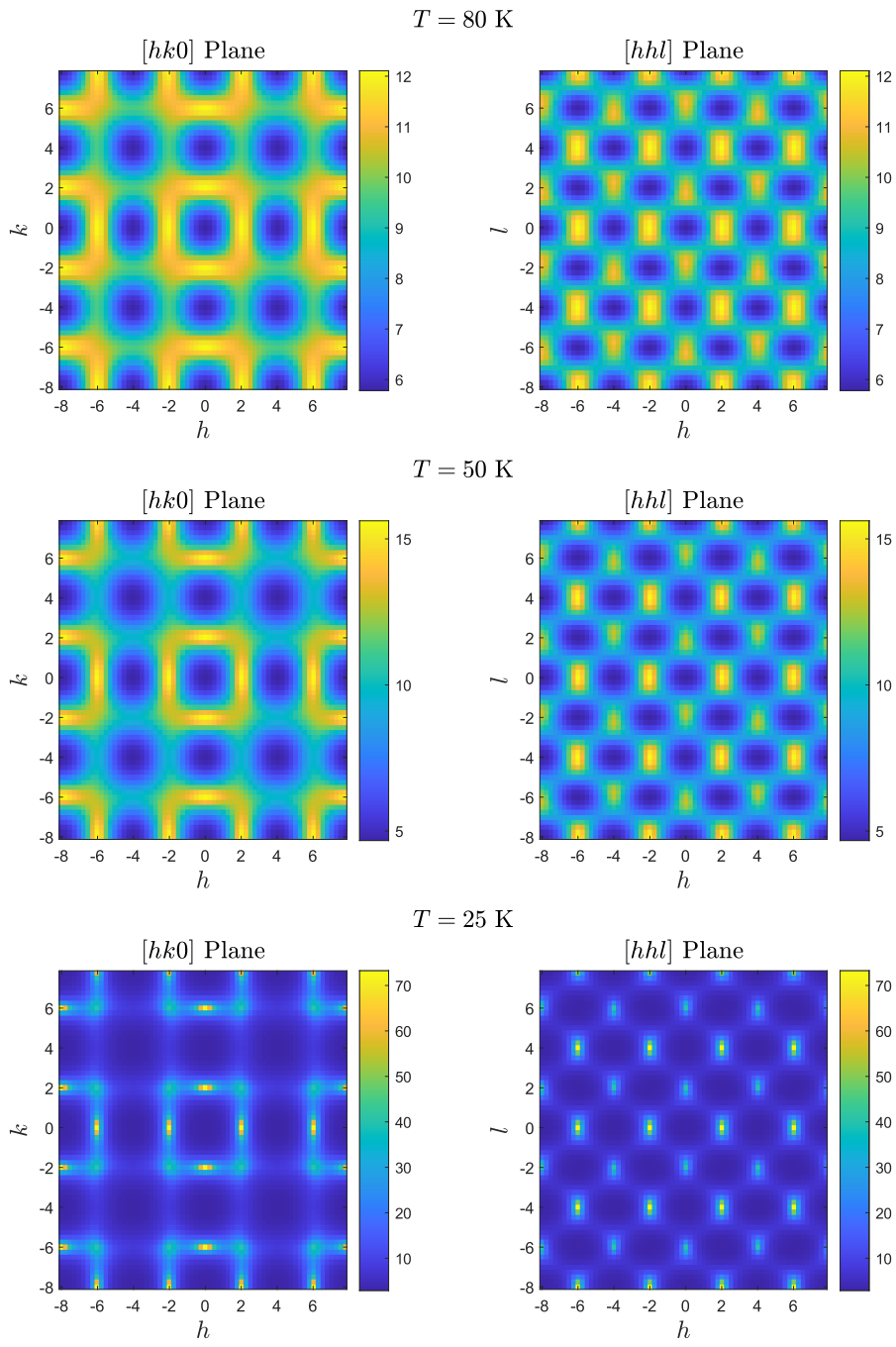


Figure 3.9: Powder average of the large- N structure factor for the up-to-3rd-NN parameters at various temperatures. The peaks, which are sharper at low temperatures, correspond to commensurate wavevectors. The dashed red vertical lines correspond to wavevectors of the form $\frac{\pi}{a}(2h, 2k, 2l)$ for integers h, k, l , which correspond to the wavevector moduli at peaks that we will see in the results from Monte Carlo simulations in Chapter 4.

Up to 5th Nearest Neighbours

Plots of the large- N structure factor for up-to-5thNN model are shown in Fig. 3.10.



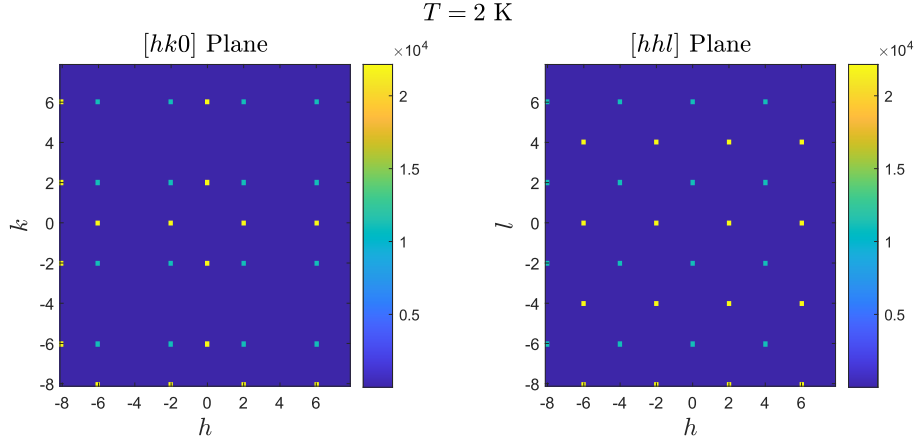


Figure 3.10: Plots of large- N structure factor with up-to-5th-NN exchange coupling at various temperatures.

The powder average, shown in Fig. 3.11, has peaks at the same wavevector moduli as the powder average for the up-to-3rd-NN parameters, which were shown in Fig. 3.9. When compared with the low-temperature powder average data for the up-to-3rd-NN model, shown in Fig. 3.9a), the peaks for up-to-5th-NN model, shown in Fig. 3.11a) become narrower in the limit of low temperatures. The reason for the difference is that the peaks in the powder average for the up-to-3rd-NN model correspond to a broad range of high-intensity wavevectors along the degeneracy line, which gives the peak a minimum width, while the peaks in the powder average for the up-to-5rd-NN model correspond to singular discrete ordering wavevectors.

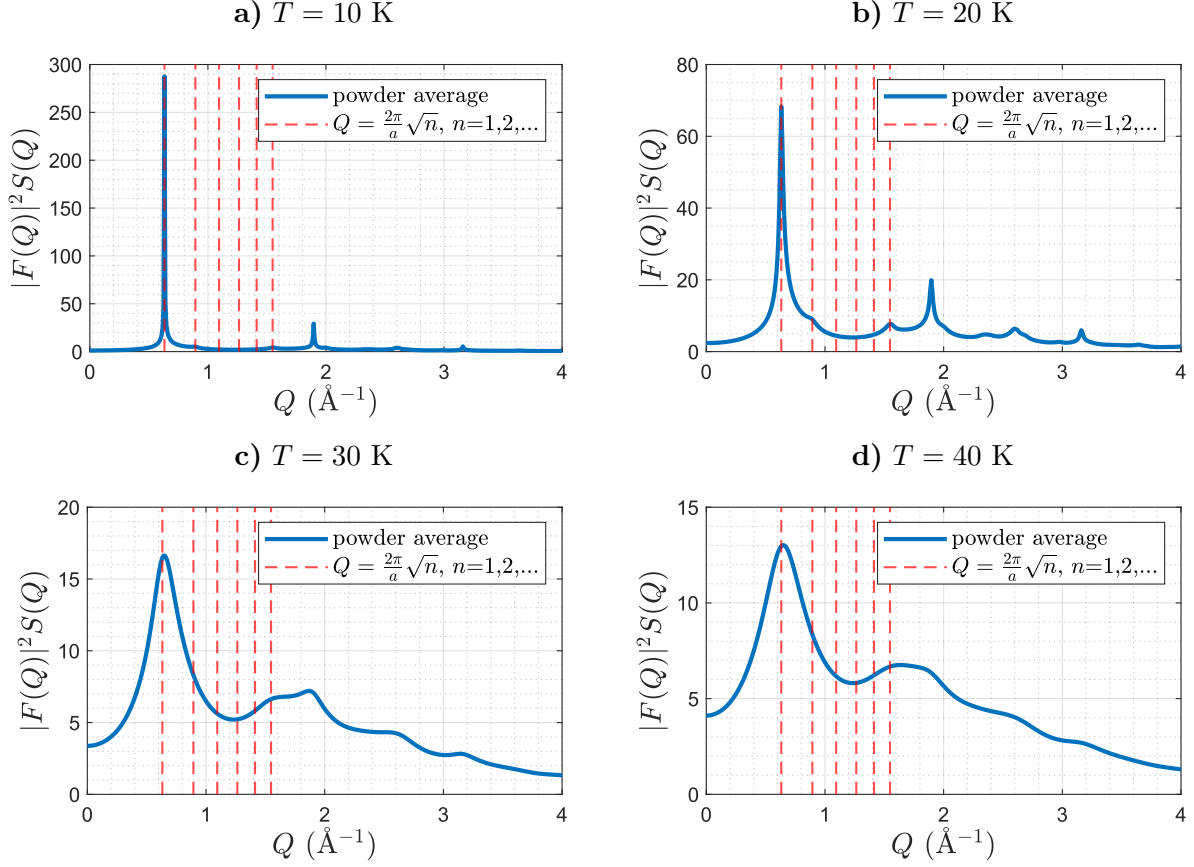


Figure 3.11: Powder average of the large- N structure factor for the up-to-5th-NN parameters at various temperatures. The peaks, which are sharper at low temperatures, are at the same wavevector moduli as the peaks in the powder average for the up-to-3rd-NN parameters. The dashed red vertical lines correspond to wavevectors of the form $\frac{\pi}{a}(2h, 2k, 2l)$ for integers h, k, l , which correspond to the wavevector moduli at peaks that we will see in the results from Monte Carlo simulations in Chapter 4.

Comparison with Collaborators

The methods presented so far are classical. To understand the effects of quantum fluctuations on the neutron scattering structure factor, our collaborators have used quantum methods called pseudo-fermion functional renormalization group (PFFRG), and pseudo-Majorana functional renormalization group (PMFRG). In PFFRG, spin operators are decomposed into products of Abrikosov fermions, more details are presented in Refs. [90–92].

The limitation of PFFRG is that the calculations can only be performed at $T = 0$. In PMFRG, the spins are instead decomposed into Majorana fermions, with consequences that allow for analysis at nonzero temperatures, as explained in Ref. [93]. Similarly to the classical MFT and large- N results, structure factors from the two quantum methods have a box pattern of high intensity in the $[hk0]$ plane. The difference, however, is that PFFRG and PMFRG give peaks along the edges of the box that are off the midpoint of the box edge. These peaks seem to be incommensurate at the available resolution, as seen in Figs. 3.12 and 3.13. The PMFRG results in Fig 3.13 further suggest that the location of these off-midpoint peaks depends on the temperature, with the peaks drawing closer to the midpoint of the box edges for higher temperatures. The temperature dependence of the peaks' locations according to PMFRG suggests that PMFRG and the classical semi-analytical methods (MFT large- N) might agree in the limit of high temperatures. From the given resolution, the peaks in the structure factor from our collaborators' PFFRG and PMFRG methods for the up-to-3rd-NN model seem to be continuous modulations along the degeneracy lines rather than being sharp Bragg peaks. This lack of Bragg peaks was seen in MFT and large- N for the same model, as shown in Figs. 3.4 and 3.8.

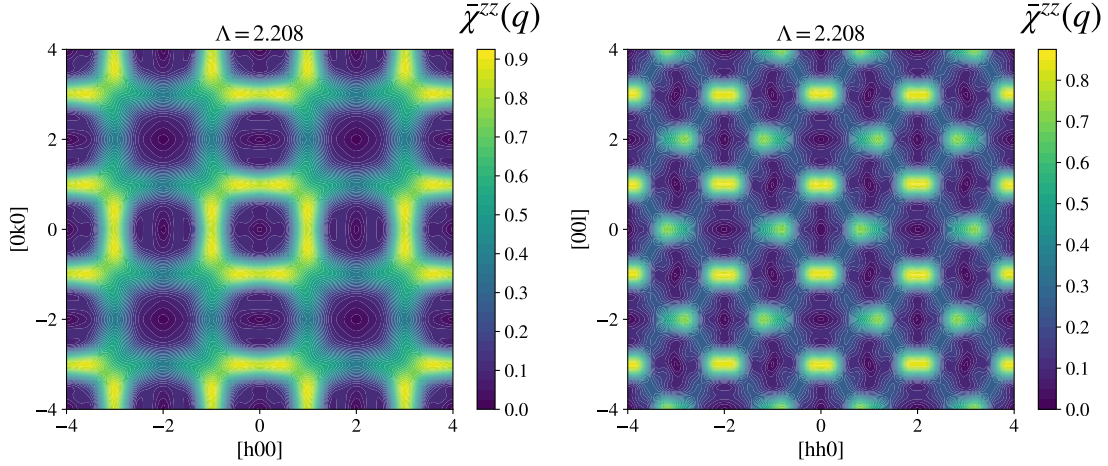


Figure 3.12: [Used with permission from Vincent Noculak, Freie Universität Berlin] PFFRG structure factor at $T = 0$ at the $[hk0]$ plane (left panel), and $[hhl]$ plane (right panel). The Hamiltonian is the up-to-3rd-NN Heisenberg model. The peaks of the structure factor in the $[hk0]$ plane (left panel) are away from but centered at the midpoint of the box edges, and the wavevector of the peaks seem to be correlated at the available resolution. Note the different convention in this plot, where the wavevectors are $\mathbf{q} = \frac{2\pi}{a}(h\hat{x} + k\hat{y} + l\hat{z})$, as opposed to the convention used for the rest of the structure factor plots in this thesis, $\mathbf{q} = \frac{\pi}{a}(h\hat{x} + k\hat{y} + l\hat{z})$ ¹.

¹Our collaborator who made Fig. 3.12 defined h, k, l as the Miller indices of a simple-cubic lattice with the cubes being the cubic supercells of the breathing pyrochlore lattice, which means that (h, k, l) are the components of the wavevectors in units of $2\pi/a$. The rest of the structure factor plots in this thesis defined h, k, l to be the components of the wavevectors in units of π/a . The convention of expressing h, k, l in units of π/a was the initial convention among our collaborators, and while the our collaborator who made Fig. 3.12 updated their convention to express h, k, l in units of $2\pi/a$, the rest of the group have kept the initial convention. While this difference in conventions between Fig. 3.12 and the rest of the structure factor plots in this thesis is confusing, we intend on standardizing the convention with our collaborators in the future. Taking the convention differences into account, the positions of the box patterns in Fig. 3.12 agree with the positions of the box patterns in the rest of the structure factor plots in this thesis for the same model (up-to-3rd-NN model).

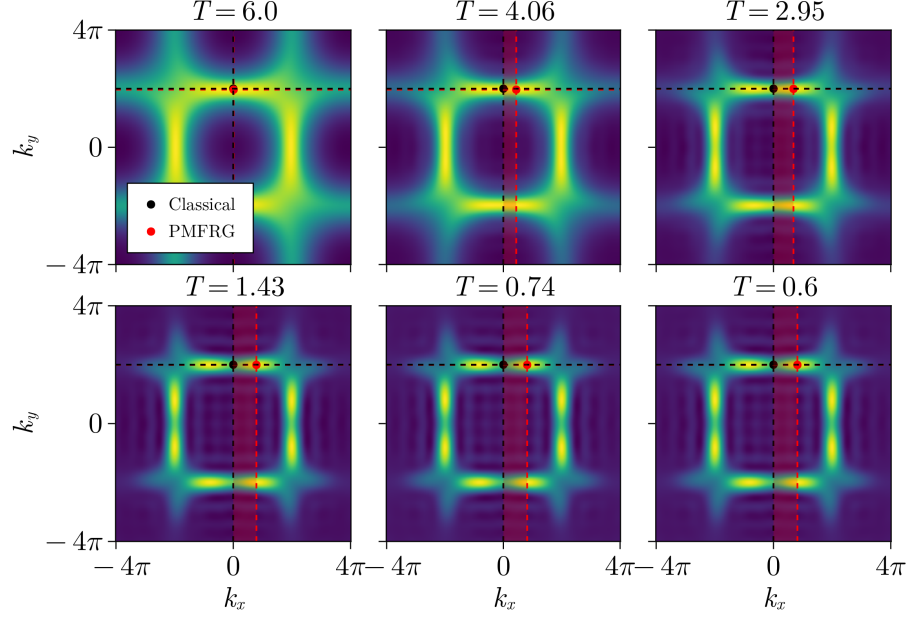


Figure 3.13: [Used with permission from Nils Niggemann, Freie Universität Berlin] PMFRG structure factor at the $[hk0]$ plane at various temperatures, using the up-to-3rd-NN Heisenberg model. Temperatures are in the unit of $J_{3a} = 6$ K. The units for the wavevectors in this figure are determined by setting $a = 1$ as the cube length in the FCC lattice translation. Similarly to PFFRG, the peaks are on the edges of the boxes and away from the midpoint of the edges. These peaks draw closer together to the midpoints of the box edges at higher temperatures, thus becoming more similar to the classical results.

In the experimental data, only the powder average is available instead of the single-crystal structure factor due to current size limitations of single crystals. In Fig. 3.14, one should observe the plots for different temperature carefully. Peaks that occur at both high and low temperatures are attributed to the structure of the lattice, while peaks that appear only at low temperatures (below the phase transition at ~ 20 K), are attributed to ordering wavevectors in the spin configurations. So far, the moduli of the ordering wavevectors do not agree with the peaks predicted by large- N , for both the up-to-3rd NN and the up-to-5th NN exchange coupling. A notable feature in the experimental data is the magnetic peak at $Q \approx 0.57 \text{ \AA}^{-1}$, which suggests a peak that is well inside the boundary of the intensity box patterns seen in all the shown theoretical methods.

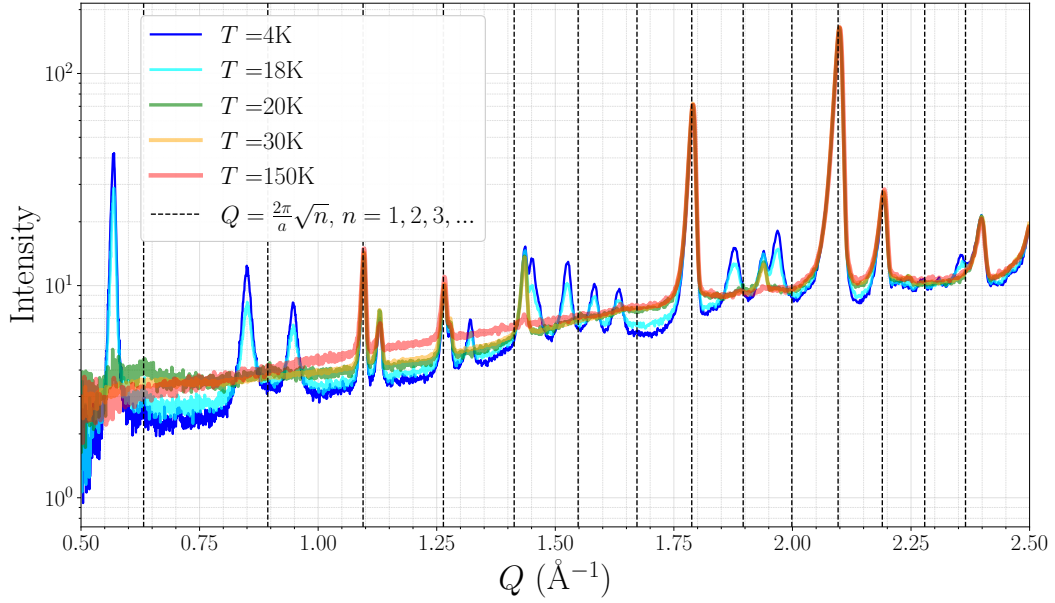


Figure 3.14: [Data included with permission from Sudarshan Sharma, McMaster University] Experimental powder average of neutron scattering in $\text{CuAlCr}_4\text{S}_8$. Blue peaks are magnetic peaks that only appear below the critical temperature, while orange peaks are structural peaks that exist due to the structure of the lattice sites rather than the orientation of the spins. Vertical dashed lines are the wavevector moduli that correspond to wavevectors of the form $\frac{\pi}{a}(2h, 2k, 2l)$ for integers h, k, l . Monte Carlo and large- N predict peaks to take place at wavevectors of that form. However, the experimental magnetic peaks disagree with the peaks predicted by large- N (and Monte Carlo simulations, whose structure factor we will see in Chapter 4).

Altered Parameters

The disagreements of the classical methods with the quantum methods, as well as the disagreements of the classical methods with the experimental data, prompted an analysis of the structure factor when the exchange parameters are altered. As it turned out, perturbations in the up-to-5th NN parameters do little in affecting the large- N structure factor, and would not change the location of the discrete commensurate energy minima without drastic changes to the exchange couplings. On the other hand, the large- N structure factor with the up-to-3rd NN coupling exchange parameters is sensitive to perturbations in the exchange coupling, as shown in Fig. 3.15.

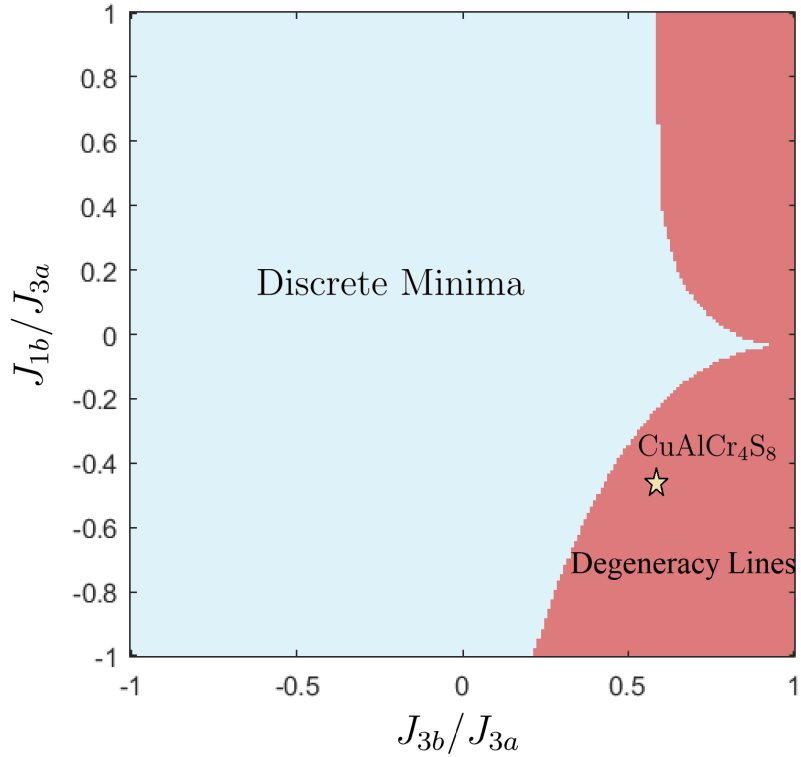


Figure 3.15: Ordering wavevector classification vs. exchange couplings J_{1b} and J_{3b} . All other up-to- J_3 couplings are fixed to the values given in Table 2.1.

Figs. 3.16 and 3.17 have a peak in the powder average for $Q < \frac{2\pi}{a} \approx 0.63 \text{ \AA}$. However, considering this is a result for altered up-to-3rd NN exchange couplings, and that the up-to-5th NN couplings have more robust peaks at the commensurate $\mathbf{Q} = \frac{2\pi}{a}(1, 0, 0)$ and

$\mathbf{Q} = \frac{2\pi}{a}(1, 1, 0)$, it is doubtful that the experimental model is just an alteration of the up-to-3rd NN exchange model.

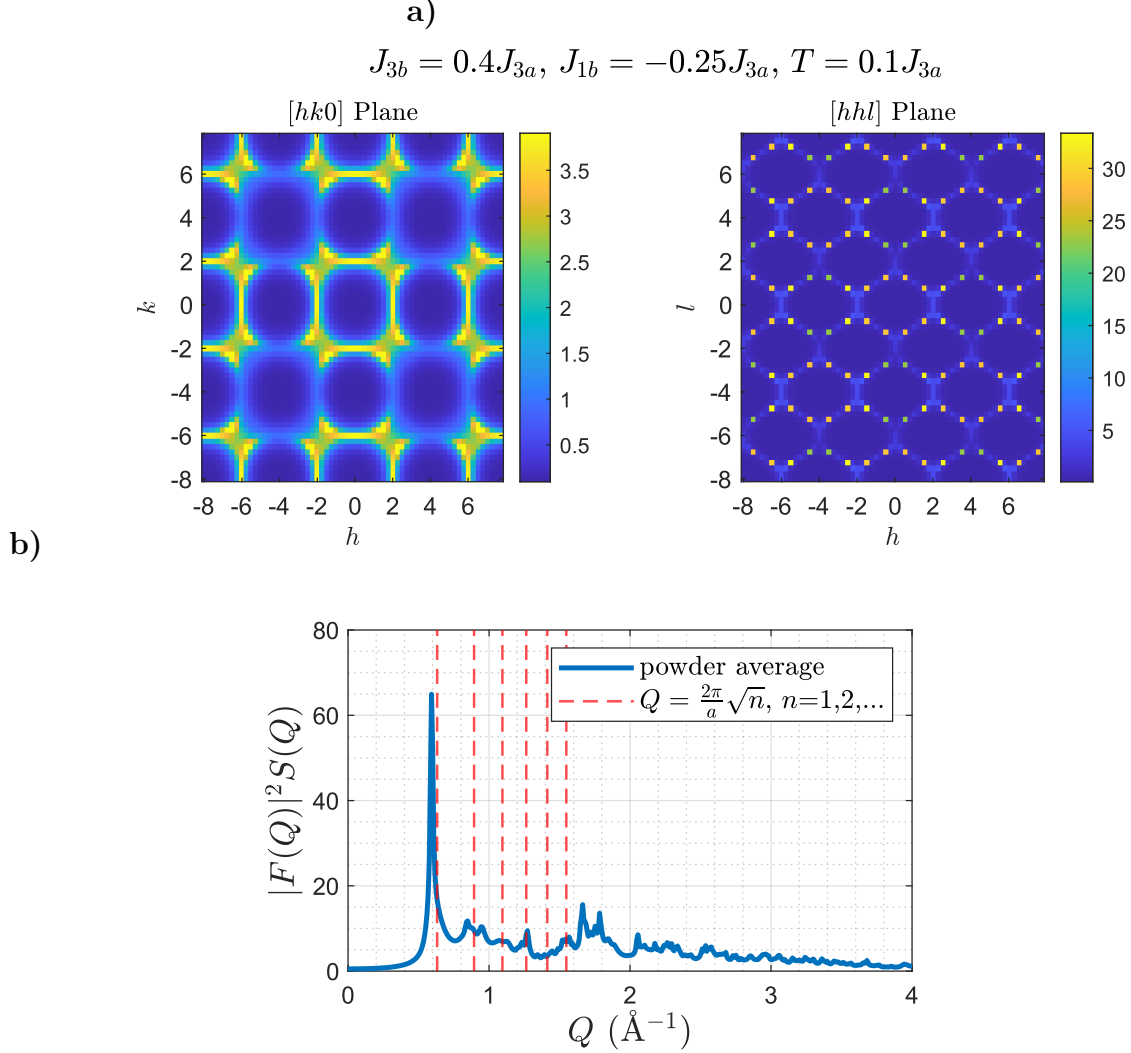


Figure 3.16: **a)** Large- N structure factor in $[hk0]$ and $[hhl]$ planes and **b)** powder average plots with exchange couplings up to J_{3b} with the alteration $J_{3b} : 0.58J_{3a} \rightarrow 0.4J_{3a}$, $J_{1b} : -0.45J_{3a} \rightarrow -0.25J_{3a}$. This set of parameters was chosen since J_{1b} , J_{3a} , and J_{3b} are the three dominant exchange couplings in the up-to-3rd-NN model and these couplings are expected to change the ordering wavevector according to the phase diagram in Fig. 3.15

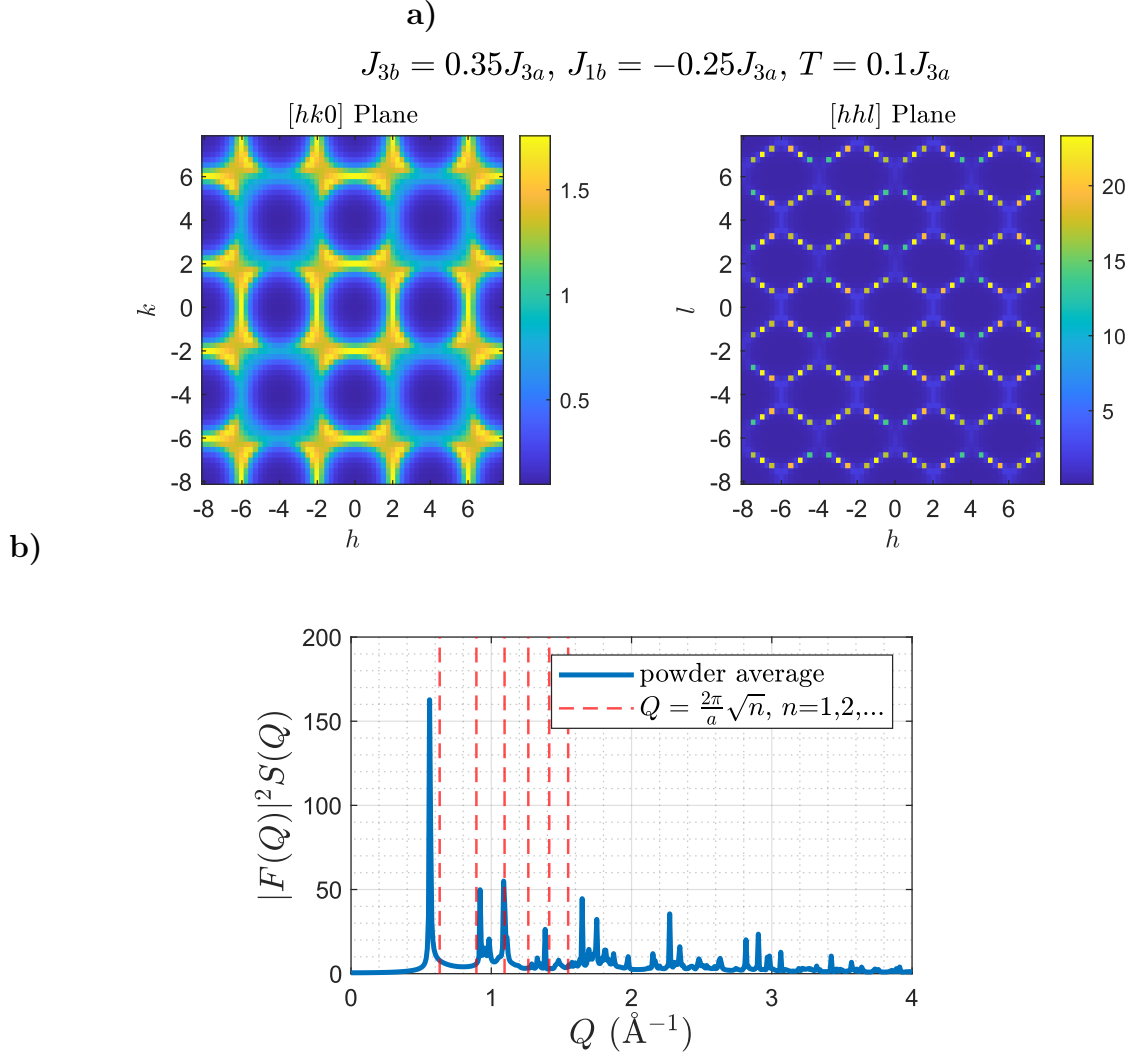


Figure 3.17: **a)** Large- N structure factor in $[hk0]$ and $[hhl]$ planes and **b)** powder average plots with exchange couplings up to J_{3b} with the alteration $J_{3b} : 0.58J_{3a} \rightarrow 0.35J_{3a}$, $J_{1b} : -0.45J_{3a} \rightarrow -0.25J_{3a}$. This alteration results in a powder average that has a magnitude below $2\pi/a$, which is a property that is seen for the first peak in the experimental powder average, shown in Fig. 3.14.

3.4 Chapter Summary

In this chapter, we presented semi-analytical methods; mean-field theory and large- N , and compared the results with our collaborating theorists and experimentalists. The classical semi-analytical methods predict peaks in the structure factor at commensurate wavevectors. The quantum methods agree in that the intensity of the structure factor is along the outline of a box, but disagree in where the peak of the structure factor is along the boundary of the box. Furthermore, the experimental data suggests there is a peak with smaller modulus than any wavevector in the intensity box. More comparisons are in the next chapter where the results from classical Monte Carlo are presented.

For the up-to-3rd-NN model, the classical semi-analytical methods (MFT and large- N) give lines of intensity along $\mathbf{q} = \pi/a(\pm 2, h, 0)$ up to permutations of the coordinates, for a real number h . While the intensity along these lines diverges to infinity as $T \rightarrow T_C^{\text{MF}}$ in MFT or $T \rightarrow 0$ in large- N , the set of high-intensity wavevectors is not a discrete set. For the AFM model on the FCC Bravais lattice, the structure factor is maximized on the same degeneracy lines [$\mathbf{q} = \pi/a(\pm 2, h, 0)$] but is constant along these lines (as shown in Fig. B.3 in Appendix B.2). On the other hand, for the up-to-3rd-NN model, the intensities along these lines vary continuously, with a maximum at $\mathbf{q} = \pi/a(\pm 2, 0, 0)$. The reason for the MFT and large- N structure factors for the up-to-3rd-NN model being maximized at $\mathbf{q} = \pi/a(\pm 2, 0, 0)$ is due to the tetrahedral unit cell's form factor.

Chapter 4

Numerical Results

In this chapter, results from classical Monte Carlo (CMC) simulations of $\text{CuAlCr}_4\text{S}_8$ as a Heisenberg model on a breathing pyrochlore are presented. Monte Carlo simulations are expected to give more accurate classical results than the semi-analytical methods used in Chapter 3. For example, for the FCC lattice, which is the underlying Bravais lattice for the breathing pyrochlore, only Monte Carlo have been shown to be useful for studying frustrated systems classically at low temperatures in Ref. [3]. As a common concern of numerical calculations of ground-states, the system has to be checked for whether it is approaching a global energy minimum rather than a local minimum at low temperatures. This concern does not materialize in the Monte Carlo simulations of the Heisenberg model on the breathing pyrochlore, which means that the implemented combination of spin sweeps and over-relaxation is ergodic with the ground state. This ergodicity has been verified for pyrochlore nearest-neighbour with FM or AFM interactions, FCC nearest-neighbours with AFM or FM couplings, $\text{CuAlCr}_4\text{S}_8$ with couplings up to J_{3b} , and $\text{CuAlCr}_4\text{S}_8$ with couplings up to J_5 . By implementing the Monte Carlo updates as sweeps defined in Section 2.5.3, a system can be assumed to be properly thermalized within ~ 100 sweeps, as can be seen Fig. 4.1.

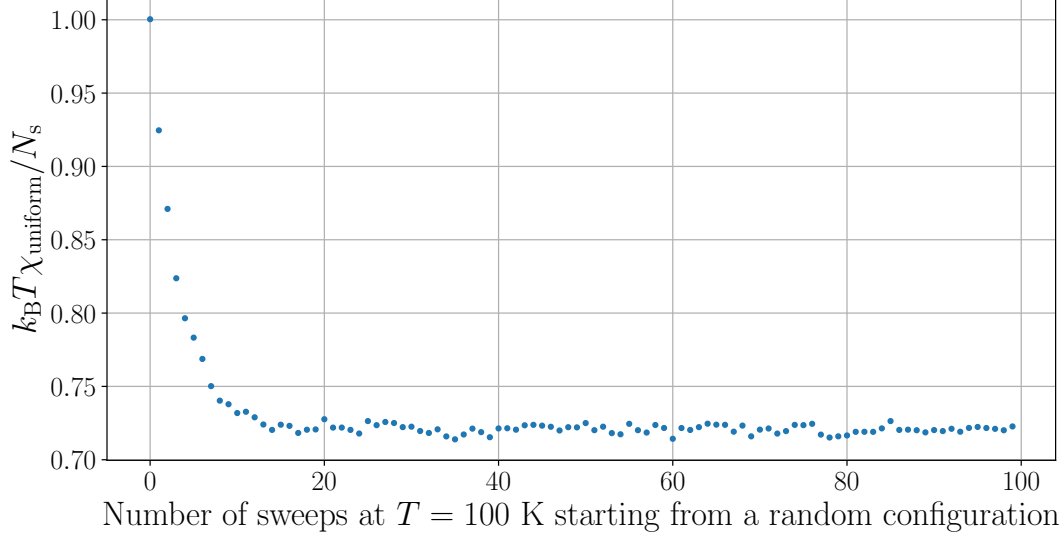


Figure 4.1: $k_B T \chi_{\text{uniform}} / N_s \approx \langle M^2 \rangle / N_s$ vs. number of Monte Carlo sweeps for $\text{CuAlCr}_4\text{S}_8$ Heisenberg model going up to J_{3b} . The system starts at a random spin configuration (as one would expect at $T = \infty$), and is thermalized at temperature 100 K. Each sweep is N_s proposed spin updates. The plot is obtained by averaging over 50,000 independent runs. As can be seen, the systems needs a few dozens of Monte Carlo sweeps to thermalize, after which the system reaches thermal equilibrium.

4.1 Specific Heat

The specific heat was calculated by using Eq. (2.27), with the energy being sampled between each Monte Carlo sweep and overrelaxation, and the sampled energies were averaged over 10,000 configurations at each temperature. When the temperature changed, the system underwent 1000 sweeps and overrelaxation updates before the energy was sampled again, to let the system thermalize.

The specific heat is a useful indicator for the existence for a phase transition and thus of a critical temperature. For the system sizes that were tested, the peaks in the specific heat are higher for larger system sizes, suggesting that they approach a singularity in the infinite-size limit. For the up-to-3rd-NN model, the critical temperature seems to converge slowly with system size, as can be seen by the left-ward shift of the peaks in Fig. 4.2a).

The critical temperature is approximately 9.9(1) K for the up-to-3rd-NN model. For the up-to-5th-NN model, the temperature of the peak converges to around 21.62(5) K, which is closer than the up-to-3rd-NN critical temperature to the experimental value of the critical temperature at around ~ 20 K. For both the up-to-3rd-NN and up-to-5th-NN models, no other distinctive features were found in the specific heat.

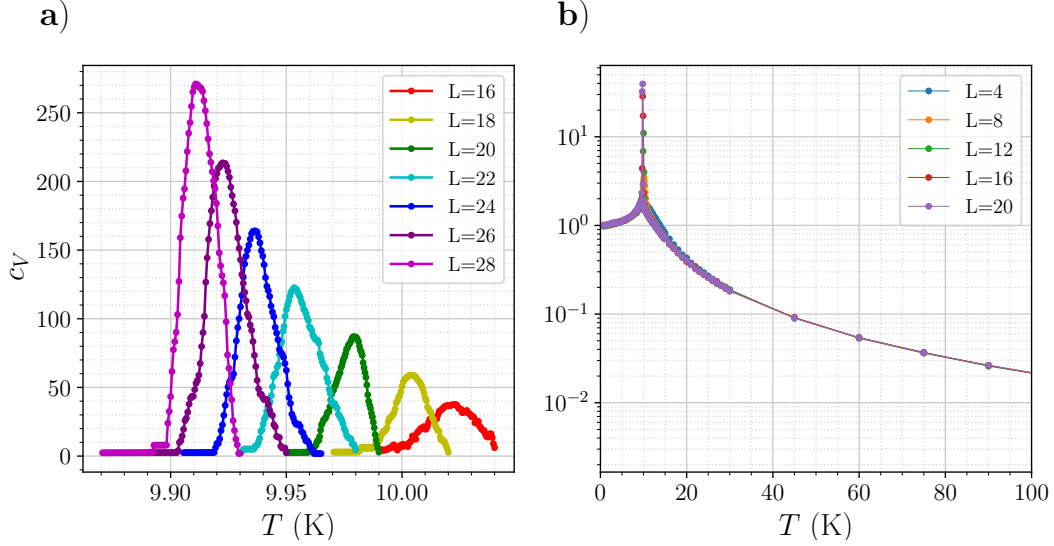


Figure 4.2: Specific heat plots for couplings up to J_{3b} , for different linear system sizes L (where there are $L \times L \times L$ unit cells) **a)** zoomed around the critical temperature **b)** zoomed out. Note that besides the peak at the critical temperature, no other features were observed at temperature range 0.1-1000 K (the range of the plot is 0.1 K- 100 K, but temperatures up to 1000 K were investigated). The growth in the height of the peaks at $T \approx 9.9(1)$ K as a function of system size suggests that the peaks represent a phase transition.

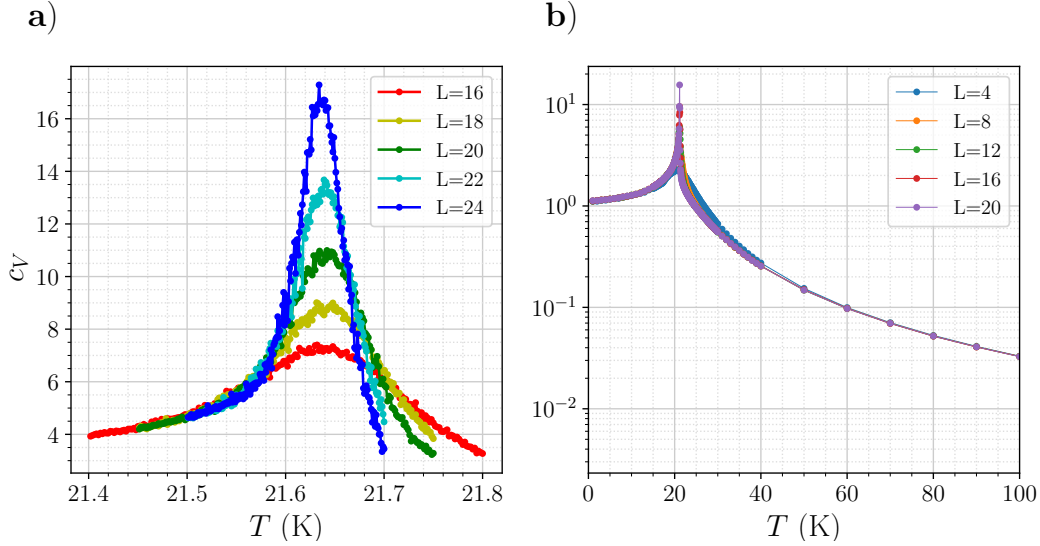


Figure 4.3: Specific heat plots for couplings up to J_5 , for different system sizes L (where there are $L \times L \times L$ unit cells) **a)** zoomed around the critical temperature **b)** zoomed out. Note that besides the peak at the critical temperature, no other features were observed at temperature range 0.1-1000 K. The growth in the height of the peaks at $T \approx 21.6(1)$ K as a function of system size suggests that the peaks represent a phase transition.

4.2 Susceptibility

The specific heat was calculated by using Eq. (2.35), and sampling the magnetization at the same time that the energy was sampled in Section 4.1 (average over 10000 configurations per temperature, with a sweep and overrelaxation between each sampling, and thermalization for 1000 sweeps+overrelaxations between each temperature change). Figs. 4.4a) and 4.5a) show that the uniform-field susceptibility has a cusp at the expected critical temperatures. The uniform-field susceptibilities do not diverge at the critical temperature, which is expected for systems with non-zero ordering wavevectors [76, 94].

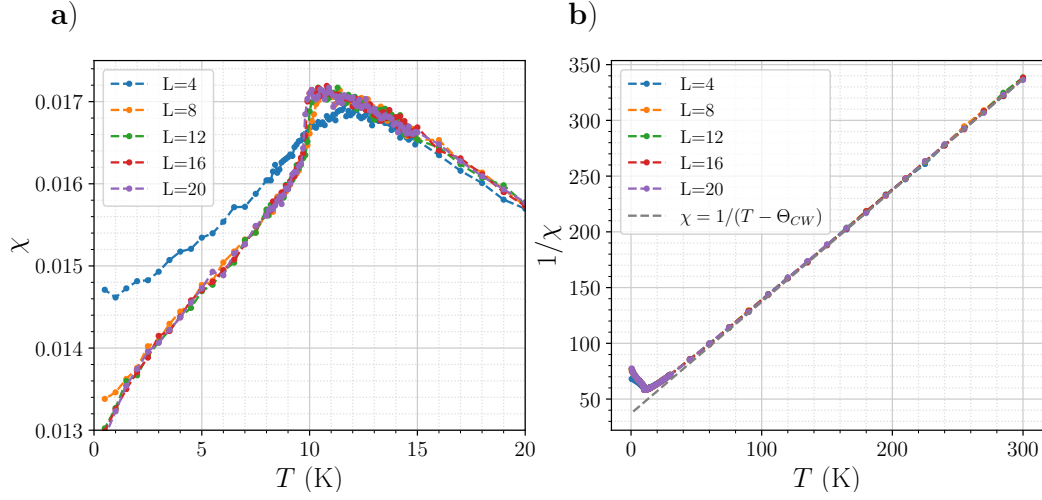


Figure 4.4: Uniform-field susceptibility at zero field. The uniform-field susceptibility is the derivative of the mean magnetization of the system with respect to the intensity of a uniform field. The classical Curie-Weiss temperature is -37.125 K

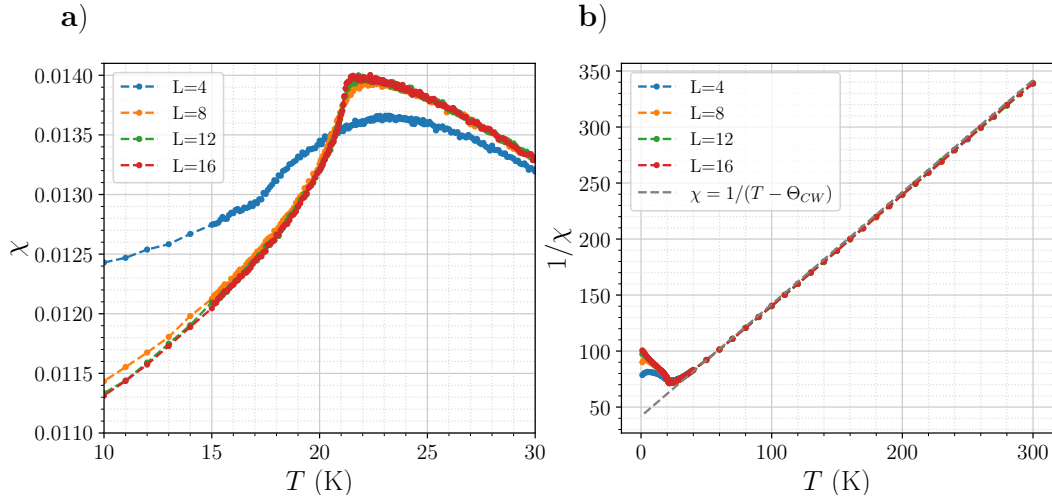


Figure 4.5: Susceptibility vs. temperature for couplings up to J_5 . Curie-Weiss temperature is -41.85 K

CMC simulations show that $T_C \ll |\Theta_{CW}|$, which confirms that the system is frustrated for both the up-to-3rd-NN and the up-to-5th-NN models [10].

4.2.1 Curie-Weiss Temperature

In Section 2.1.3, we derived the Curie-Weiss law at *high* temperatures

$$\frac{1}{\chi} \propto (T - \Theta_{\text{CW}}), \quad (4.1)$$

where

$$\Theta_{\text{CW}} = -\frac{S^2}{3} \sum_j \mathcal{J}_{ij} \quad (4.2)$$

for a fixed site index i , with the convention that $\mathcal{J}_{ij} > 0$ for an antiferromagnetic Heisenberg exchange coupling, and $S = 3/2$ for Cr^{3+} . From large- N and CMC simulations, which were the methods for which susceptibility was calculated, the susceptibility data of these methods at high temperatures agrees with Eq. (4.1) for the value of Θ_{CW} defined in Eq. (4.2). The values are $\Theta_{\text{CW}} = -37.125$ K for the up-to-3rd-NN model, and $\Theta_{\text{CW}} = -41.85$ K for the up-to-5th-NN model. However, the value of Θ_{CW} defined in Eq. (4.2) assumes that the spin- S 's have a modulus S^2 , due to the spins being treated as classical in large- N and CMC simulations. When taking quantum mechanics into consideration, the modulus of a spin- S becomes $S(S+1)$. This means that the quantum-mechanical Curie Weiss temperature, $\Theta_{\text{CW}}^{\text{q}}$, can be expressed by replacing S^2 in Eq. (4.2) by $S(S+1)$ to give

$$\Theta_{\text{CW}}^{\text{q}} = -\frac{S(S+1)}{3} \sum_j \mathcal{J}_{ij}, \quad (4.3)$$

which for our models can be simplified to

$$\Theta_{\text{CW}}^{\text{q}} = -\frac{S(S+1)}{3} [3(J_{1a} + J_{1b}) + 12J_2 + 6(J_{3a} + J_{3b} + J_4 + J_5)]. \quad (4.4)$$

Using Eq. (4.4), with the exchange couplings given in Table 3.1, the spin-modulus-corrected Curie-Weiss temperatures are $\Theta_{\text{CW}}^{\text{q}} = -61.875$ K for the up-to-3rd-NN model and $\Theta_{\text{CW}}^{\text{q}} = -69.75$ K for the up-to-5th-NN model, while the experimental value is -68.7(9) K [33]. To summarize, the Curie-Weiss temperatures predicted by classical data [Eq. (4.2)] disagree with experimental data due to the assumptions that the spins are classical. When correcting the moduli of the spins to be in line with quantum mechanics, the Curie-Weiss temperatures are scaled by a factor of $(S+1)/S = 5/3$ to give values that are closer to the experimental Curie-Weiss temperature, with the up-to-5th-NN model giving a closer value to experiment after correcting the moduli of the spins.

4.3 Structure Factor

In this section, we will present the single-crystal structure factors from Monte Carlo simulations. Due to time constraints, the powder average of the structure factor has not been calculated from Monte Carlo simulations of the theoretical models of $\text{CuAlCr}_4\text{S}_8$ at the time of writing this thesis. Despite the absence of Monte Carlo powder average, the wavevector moduli at peaks in the would-be powder average can be obtained from the single-crystal structure factor.

Up to 3rd Nearest Neighbours

Structure factor at various temperatures are plotted for the $[hk0]$ plane at Fig. 4.6 and the $[hhl]$ plane at Fig. 4.7.

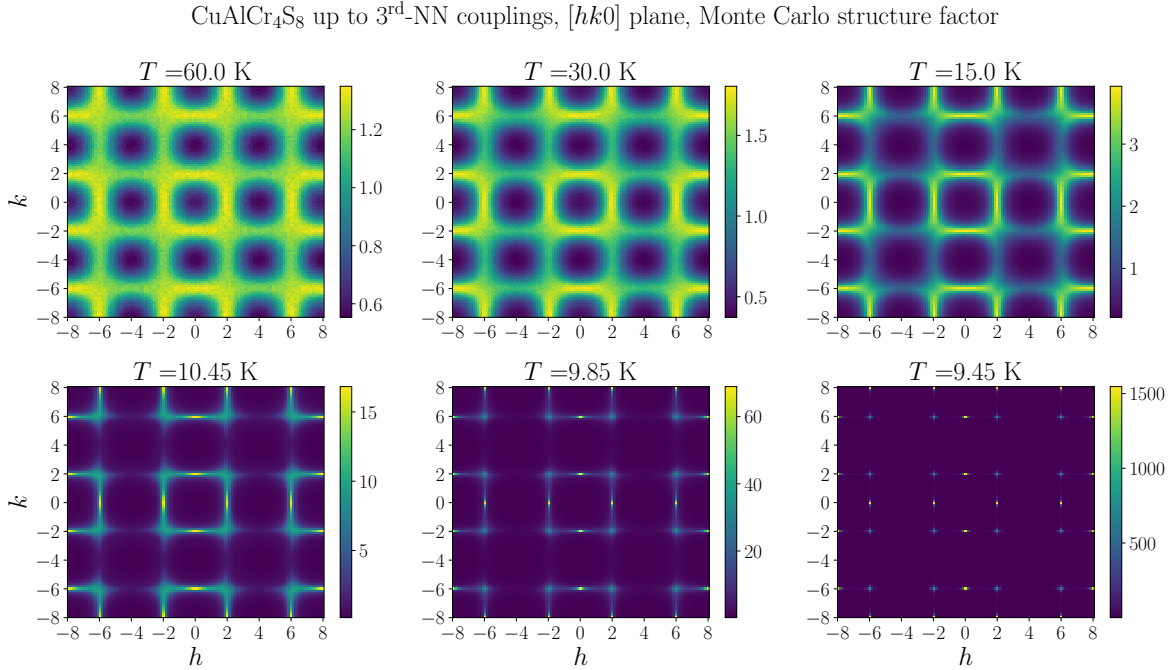


Figure 4.6: Structure factor along the $[hk0]$ plane for system size $28 \times 28 \times 28$ unit cells, when including exchange couplings up to J_{3b} . The wavevector represented by $[hk0]$ is $\mathbf{Q} = \frac{\pi}{a}(h\hat{x} + k\hat{y})$

CuAlCr₄S₈ up to 3rd-NN couplings, $[hhl]$ plane, Monte Carlo structure factor

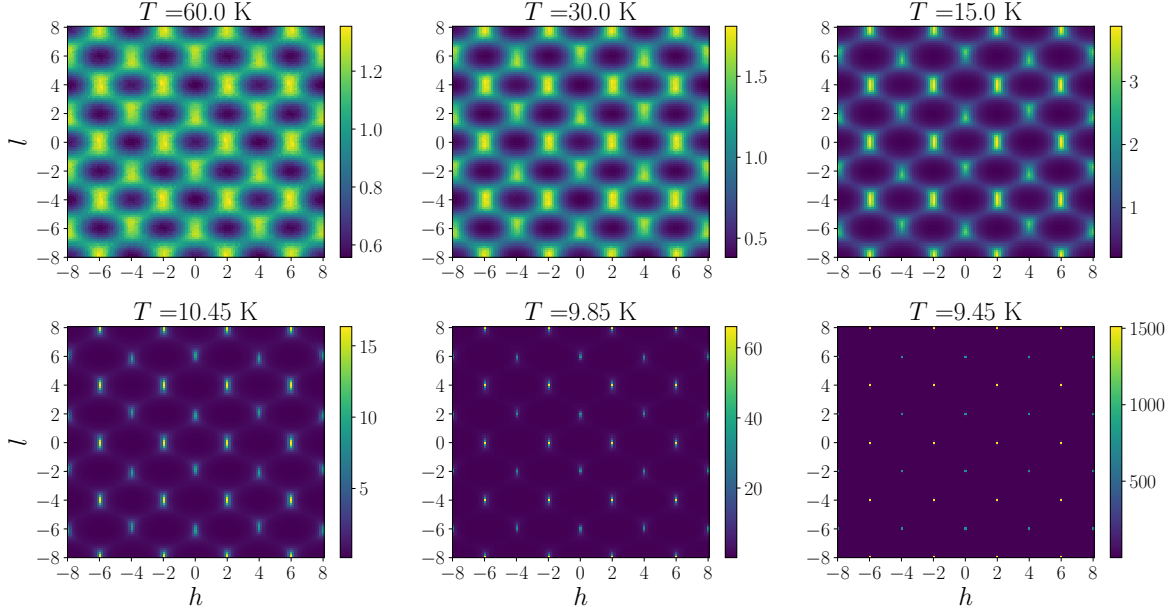


Figure 4.7: Structure factor along the $[hhl]$ plane for system size $28 \times 28 \times 28$ unit cells, when including exchange couplings up to J_{3b} . The wavevector represented by $[hhl]$ is $\mathbf{Q} = \frac{\pi}{a}(h\hat{x} + h\hat{y} + l\hat{z})$

The nature of the peaks of the form $\mathbf{Q} = 2\pi/a(\pm 1, 0, 0)$ and $\mathbf{Q} = 2\pi/a(\pm 1, \pm 1, 0)$ is investigated in Fig. 4.8, where the structure factor in the $[hk0]$ plane is plotted at a very low temperature ($0.01\text{K} \sim 10^{-3}\text{K}$). The peaks only seem to become sharper for larger system sizes, suggesting that they are Bragg peaks. Since these peaks are a discrete subset of the degeneracy line that is the ground state manifold, this suggests that the peaks are due to order by disorder (ObD). Rather than have the ordering wavevector be anywhere along the degeneracy line $\mathbf{Q} = 2\pi/a(1, k, 0)$, the ordering wavevector takes place at the intersections of degeneracy lines. The ObD mechanism favours the intersections of the degeneracy lines due to the greater availability of modes of thermal fluctuations [3].

Even though MFT, large- N and CMC simulations all show structure factor peaks at the same wavevectors, $\mathbf{Q} = 2\pi/a(\pm 1, 0, 0)$ up to permutations of the coordinates, the nature of the peaks is different in CMC simulations. While MFT and large- N also gave structure factor peaks at $\mathbf{Q} = 2\pi/a(\pm 1, 0, 0)$, these peaks were within a degeneracy line of wavevectors that had a diverging intensity at low temperatures ($T \rightarrow T_C^{\text{MF}}$ for MFT,

$T \rightarrow 0$ for large- N). Moreover, the maximum of the structure factors from MFT and large- N at $\mathbf{Q} = 2\pi/a(\pm 1, 0, 0)$ is a maximum due to the tetrahedral unit-cell's form factor, and the structure factor along the degeneracy line is uniform in the absence of the form factor (as is the case for AFM model on the FCC lattice, shown in Fig. B.3 in Appendix B.2). The structure factor peaks from CMC simulations at $\mathbf{Q} = 2\pi/a(\pm 1, 0, 0)$ and $\mathbf{Q} = 2\pi/a(\pm 1, \pm 1, 0)$ have a different nature from the peaks from MFT and large- N , since the peaks from CMC simulations are discrete, where the intensity away from those peaks vanishes even along the degeneracy line.

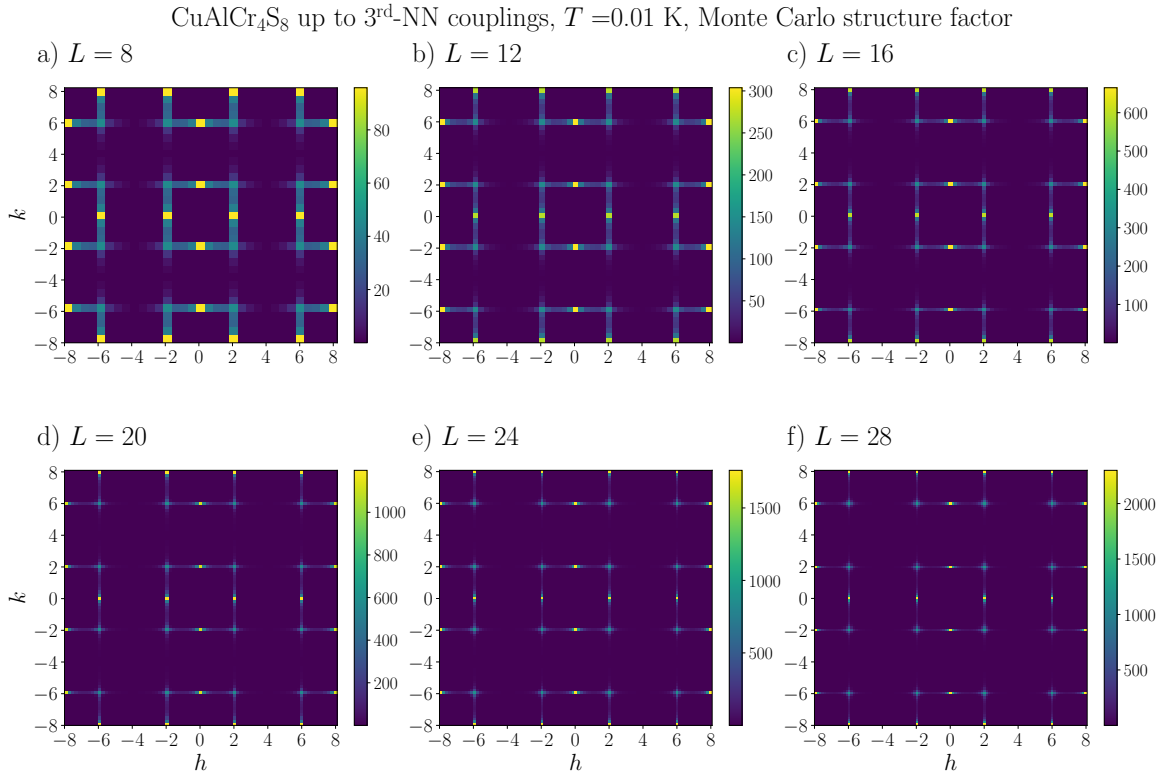


Figure 4.8: Structure factor in the $[hk0]$ plane at temperature $T \sim 10^{-3}T_C$ including couplings up to J_{3b} . Despite the degeneracy line, there are peaks that sharper as the system size increases, suggesting Bragg peaks. These Bragg peaks also happen for the Bravais lattice analogue, the FCC, as discussed in Appendix B.

Up to 5th Nearest Neighbours

Structure factor at various temperatures are plotted for the $[hk0]$ plane at Fig. 4.9 and the $[hhl]$ plane at Fig. 4.10.

CuAlCr₄S₈ up to 5th-NN couplings, $[hk0]$ plane, Monte Carlo structure factor

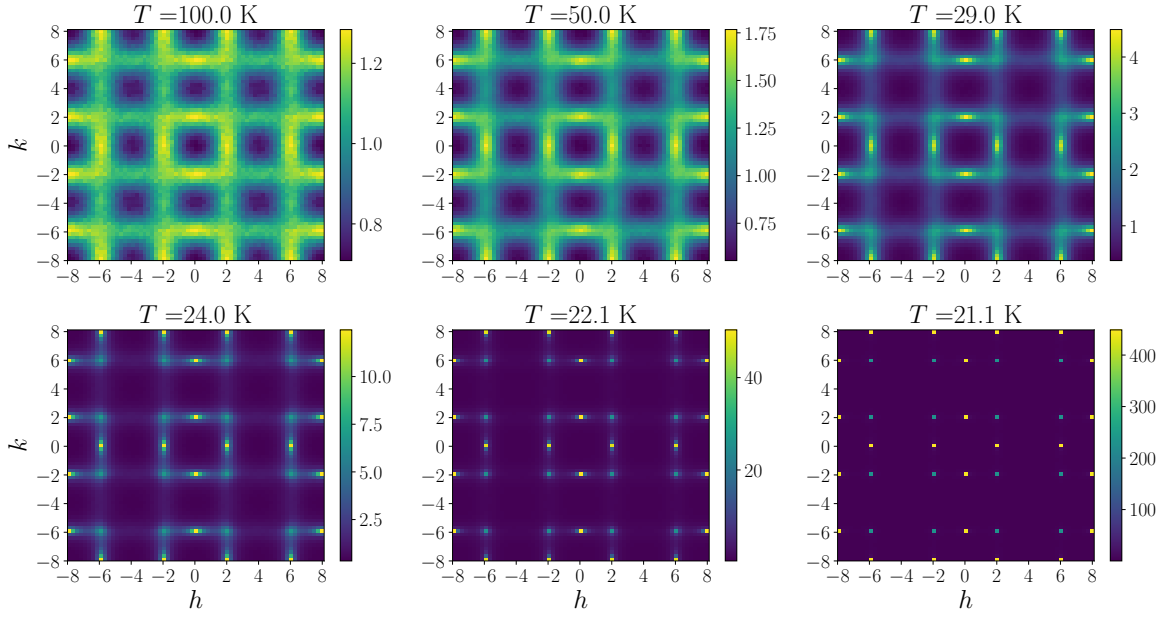


Figure 4.9: Structure factor along the $[hk0]$ plane for system size $16 \times 16 \times 16$ unit cells, when including exchange couplings up to J_5 . The wavevector represented by $[hk0]$ is $\mathbf{Q} = \frac{\pi}{a}(h\hat{x} + k\hat{y})$.

CuAlCr₄S₈ up to 5th-NN couplings, $[hhl]$ plane, Monte Carlo structure factor

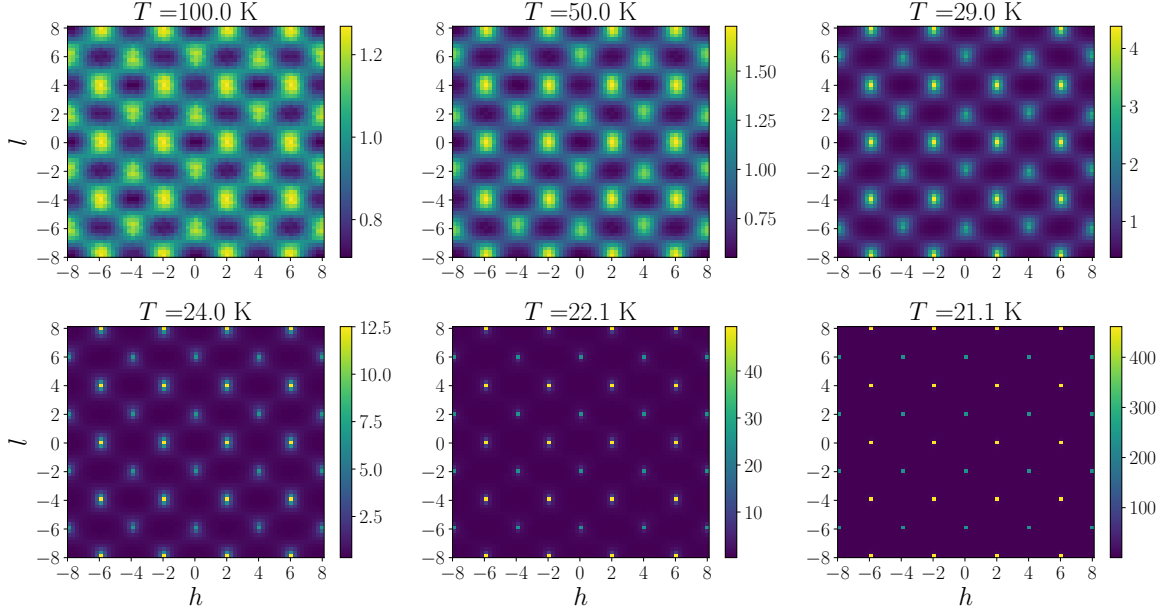


Figure 4.10: Structure factor along the $[hhl]$ plane for system size $16 \times 16 \times 16$ unit cells, when including exchange couplings up to J_5 . The wavevector represented by $[hhl]$ is $\mathbf{Q} = \frac{\pi}{a}(h\hat{x} + h\hat{y} + l\hat{z})$.

Altered Parameters

In Section 3.3.2, we examined the effect of altering the exchange parameters in the up-to-3rd-NN set of parameters. Recall from Section 3.3.2 that changes to the up-to-5th-NN parameters do not alter the ordering wavevector unless the changes in the dominant exchange couplings (J_{3a} , J_{3b} , and J_{1b}) are drastic (such as changes by 100%). Thus, we only show the results for alterations of the up-to-3rd-NN parameters. Figs. 4.11-4.14 show that slight alterations in the up-to-3rd-NN couplings can alter the structure factor. Figs. 4.12 and 4.14 show an agreement between the CMC structure factor and the large- N structure factor, but Figs. 4.11 and 4.13 do not. The disagreement between the large- N and CMC structure factors could be due thermal fluctuations that are captured in CMC simulations but not in large- N . Even with the altered parameters, While the temperatures for Figs. 4.11-4.14 are at $T = 0.1J_{3a}$, which an order of magnitude lower than the critical temperature from the unaltered up-to-3rd-NN model's Monte Carlo simulations ($T_C \sim J_{3a}$),

the new discrete minima that emerge might be too shallow to be strongly-selected, even at temperatures as low as $0.1J_{3a}$. For example, if a state at the blue region in the phase diagram in Fig. 4.11a) has an energy separation that is $\lesssim 0.1J_{3a}$ from the ground state, it would still be a thermally probable state at $T = 0.1J_{3a}$, especially if it has a high entropy, such as a state with a large degeneracy. Despite the disagreements between the structure factors from large- N and CMC simulations at $T = 0.1J_{3a}$ from Figs. 4.11 and 4.13, the point that the ordering wavevector in the up-to-3rd-NN model is sensitive to alterations of its exchange coupling parameters still holds.

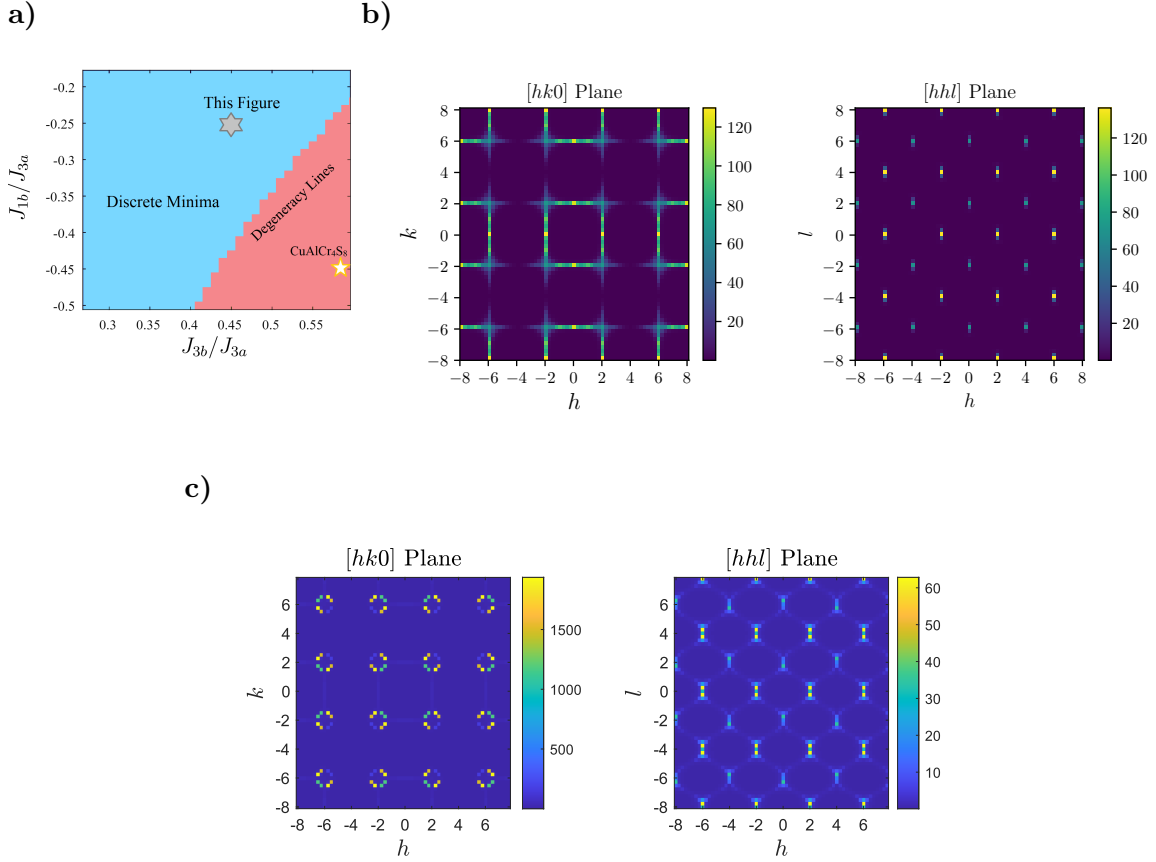


Figure 4.11: **a)** Phase diagram from Fig. 3.15, with the parameters for the up-to-3rd-NN model for CuAlCr₄S₈ marked as a yellow star $[(J_{3b}/J_{3a}, J_{1b}/J_{3a}) \approx (0.58, -0.45)]$, and the parameters in this figure marked in a gray star $[(J_{3b}/J_{3a}, J_{1b}/J_{3a}) = (0.45, -0.25)]$. **b)** Monte Carlo and **c)** large- N structure factor plots for system with $16 \times 16 \times 16$ unit cells at $T = 0.1J_{3a} \approx 0.6$ K.

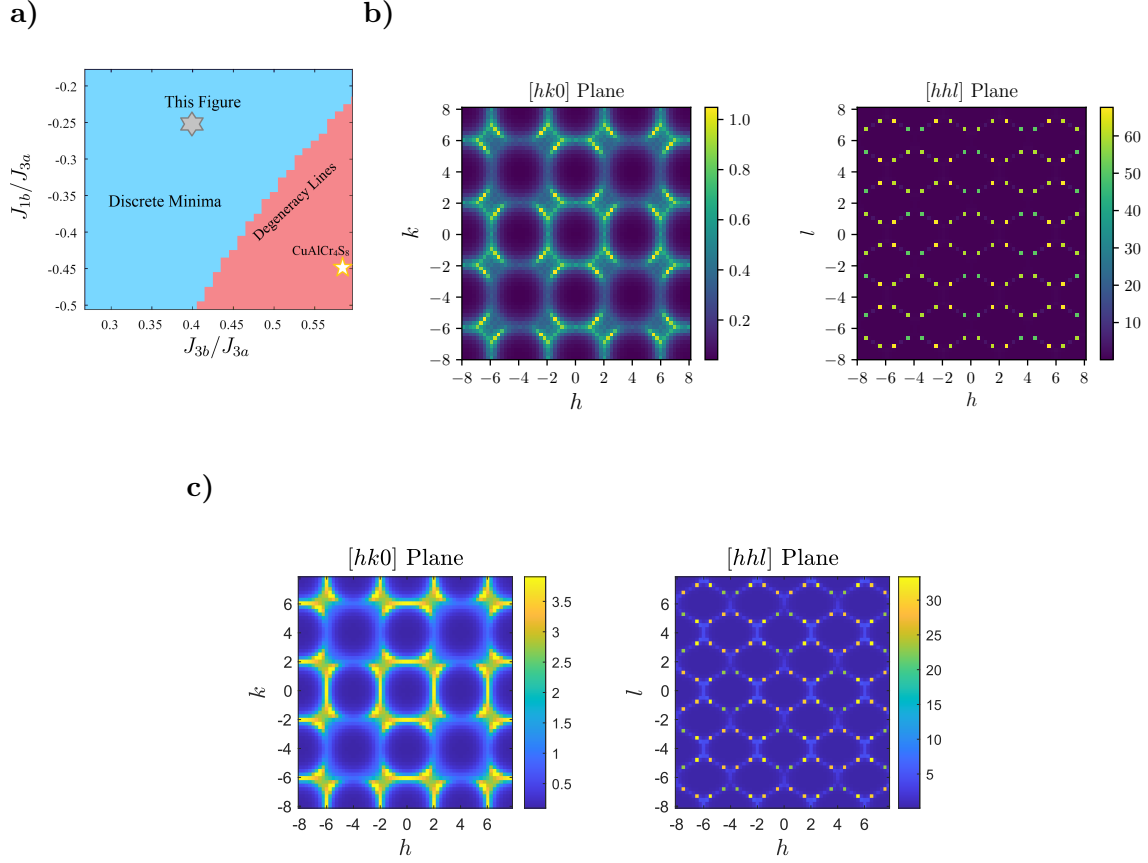


Figure 4.12: **a)** Phase diagram from Fig. 3.15, with the parameters for the up-to-3rd-NN model for CuAlCr₄S₈ marked as a yellow star [$(J_{3b}/J_{3a}, J_{1b}/J_{3a}) \approx (0.58, -0.45)$], and the parameters in this figure marked in a gray star [$(J_{3b}/J_{3a}, J_{1b}/J_{3a}) = (0.4, -0.25)$]. **b)** Monte Carlo and **c)** large- N structure factor plots for system with $16 \times 16 \times 16$ unit cells at $T = 0.1J_{3a} \approx 0.6$ K.

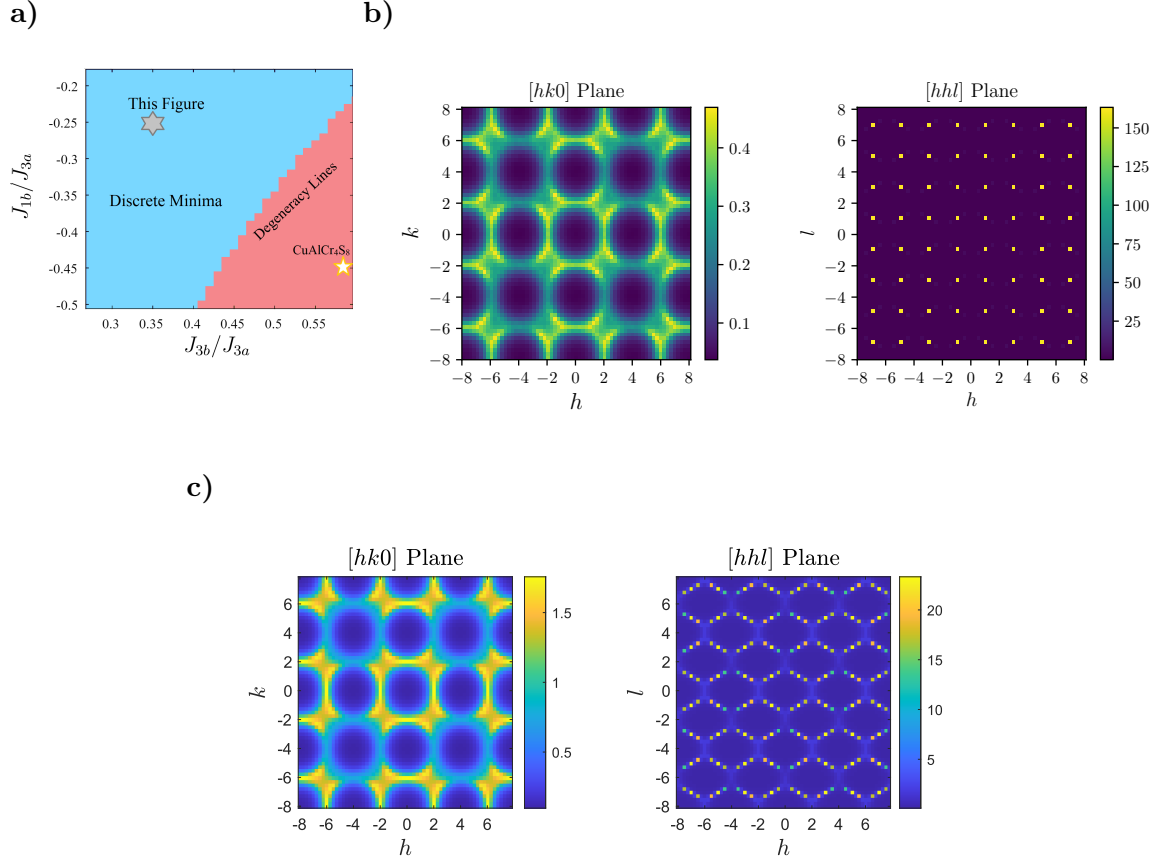


Figure 4.13: **a)** Phase diagram from Fig. 3.15, with the parameters for the up-to-3rd-NN model for CuAlCr₄S₈ marked as a yellow star [$(J_{3b}/J_{3a}, J_{1b}/J_{3a}) \approx (0.58, -0.45)$], and the parameters in this figure marked in a gray star [$(J_{3b}/J_{3a}, J_{1b}/J_{3a}) = (0.35, -0.25)$]. **b)** Monte Carlo and **c)** large- N structure factor plots for system with $16 \times 16 \times 16$ unit cells at $T = 0.1J_{3a} \approx 0.6$ K.

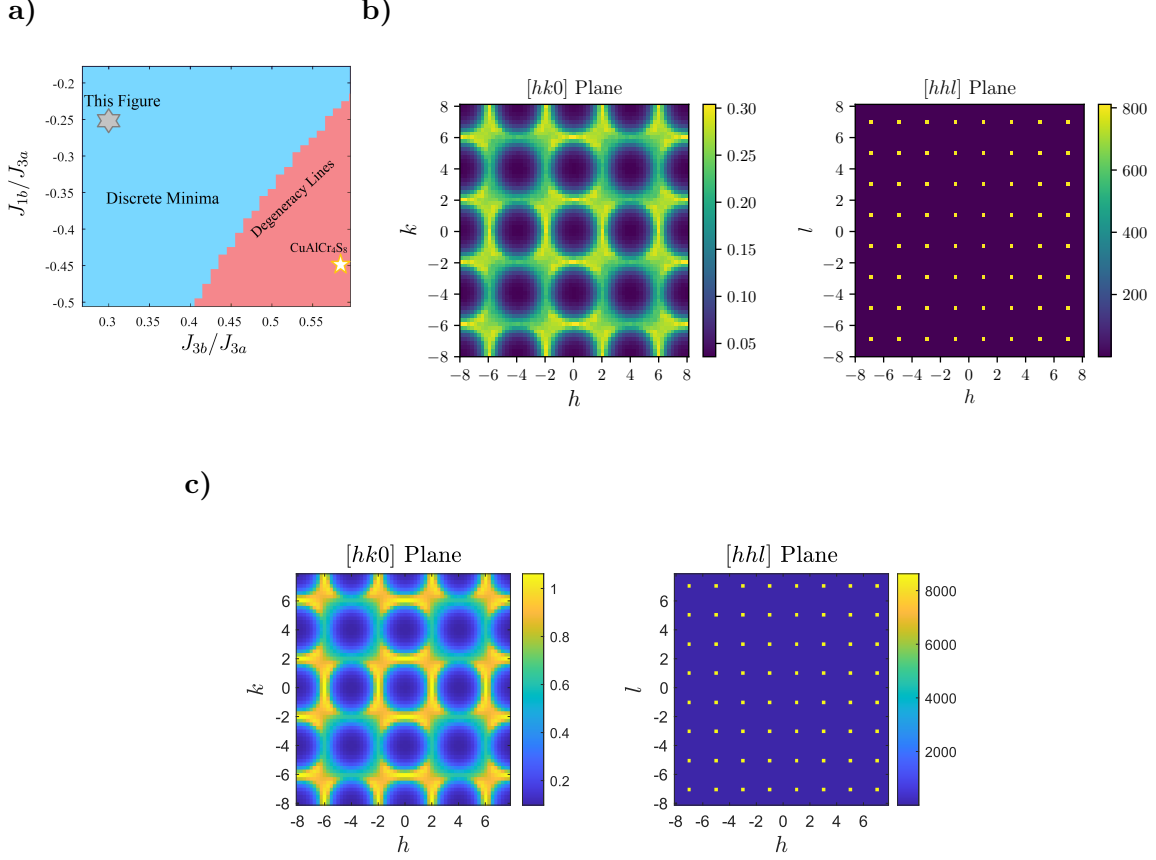


Figure 4.14: **a)** Phase diagram from Fig. 3.15, with the parameters for the up-to-3rd-NN model for CuAlCr₄S₈ marked as a yellow star $[(J_{3b}/J_{3a}, J_{1b}/J_{3a}) \approx (0.58, -0.45)]$, and the parameters in this figure marked in a gray star $[(J_{3b}/J_{3a}, J_{1b}/J_{3a}) = (0.3, -0.25)]$. **b)** Monte Carlo and **c)** large- N structure factor plots for system with $16 \times 16 \times 16$ unit cells at $T = 0.1J_{3a} \approx 0.6$ K.

4.4 Real-Space Spin Configurations

While the lattices have been mostly investigated by the structure factor in momentum space, there is importance in inspecting the spins in real space. This is so because there could be many different ground states that have different properties but have the same structure factor. Such differences would only be observable when looking at the real-space configurations of the spins. Individual spin configurations were obtained at low

temperature $T \sim 0.001T_C$. The systems started as random spin configurations and were given 2000 sweeps and overrelaxations at $T \sim 0.001T_C$ to thermalize. The systems shown in Figs. 4.15 and 4.16 are cubic supercells from a $16 \times 16 \times 16$ system. The energies of the configurations were all confirmed to have an energy equal to the ground state energy, within negligible thermal fluctuations.

The up-to-3rd-NN Heisenberg model has ground states with spirals, where the wavevector needs not be commensurate with the Brillouin-Zone dimensions $2\pi/a$. As a result, the spins may form patterns that do not have periods that fit within a whole number of unit cells, and instead the spins seem to twist in a spiral, as can be seen in Fig. 4.15.

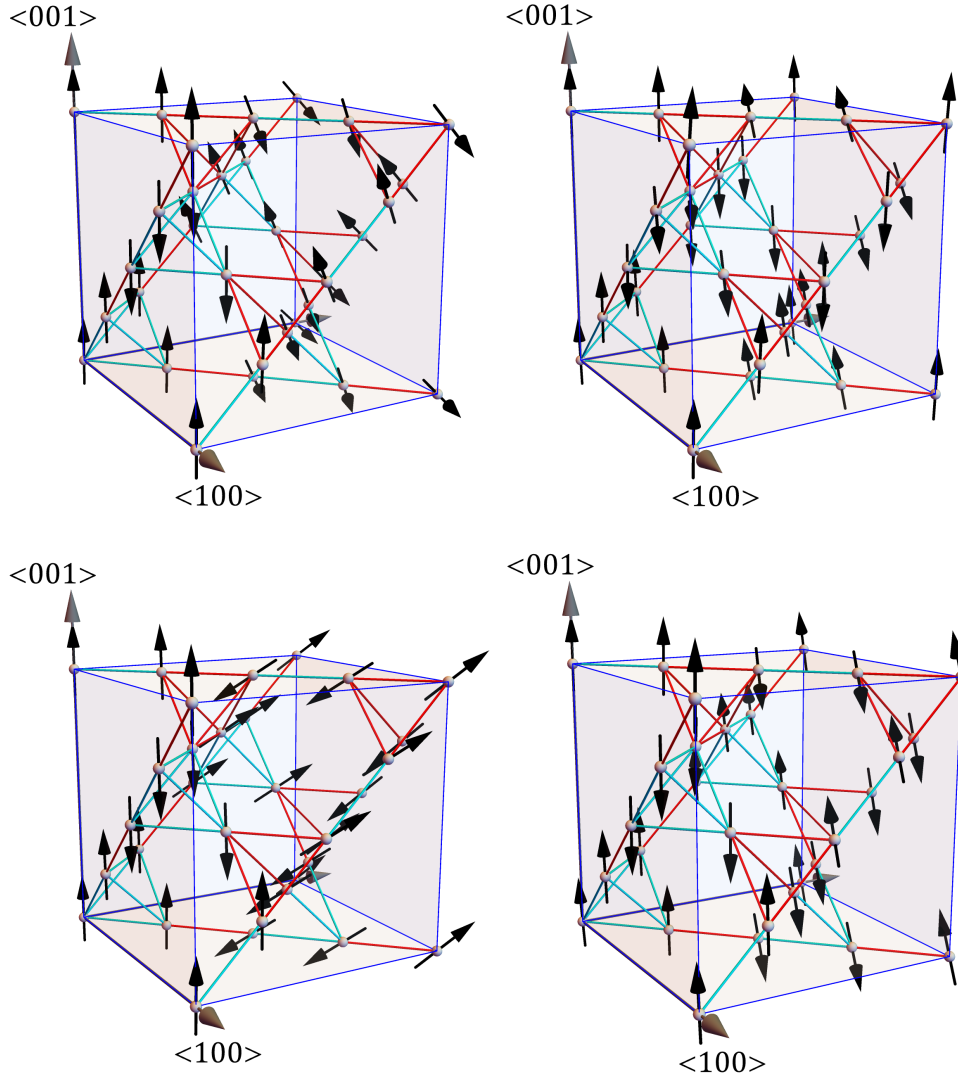


Figure 4.15: Four cubic supercells from four different $16 \times 16 \times 16$ unit cell systems from CMC simulations of the up-to-3rd-NN model. Each cubic cell is from a different system thermalized at $0.01\text{K} \sim 10^{-3}T_C$. Note that with the exception of the configuration in the top-right, the spins on the corners of the boxes point in different directions, suggesting some contribution from wavevectors that are not $\frac{2\pi}{a}(\pm 1, \pm 1, 0)$ or $\frac{2\pi}{a}(\pm 1, 0, 0)$. As suggested by the structure factors shown in Fig 4.8, the selection of the $\frac{2\pi}{a}(\pm 1, \pm 1, 0)$ or $\frac{2\pi}{a}(\pm 1, 0, 0)$ ordering wavevectors should become more dominant for larger systems.

On the other hand, the ground-state degeneracy in momentum space is broken when updating the model to the up-to-5th-NN model, and lead to energy ground states at the commensurate $\mathbf{Q} = \frac{2\pi}{a}(\pm 1, 0, 0)$ or $\frac{2\pi}{a}(\pm 1, \pm 1, 0)$, as can be seen in Fig. 4.16.

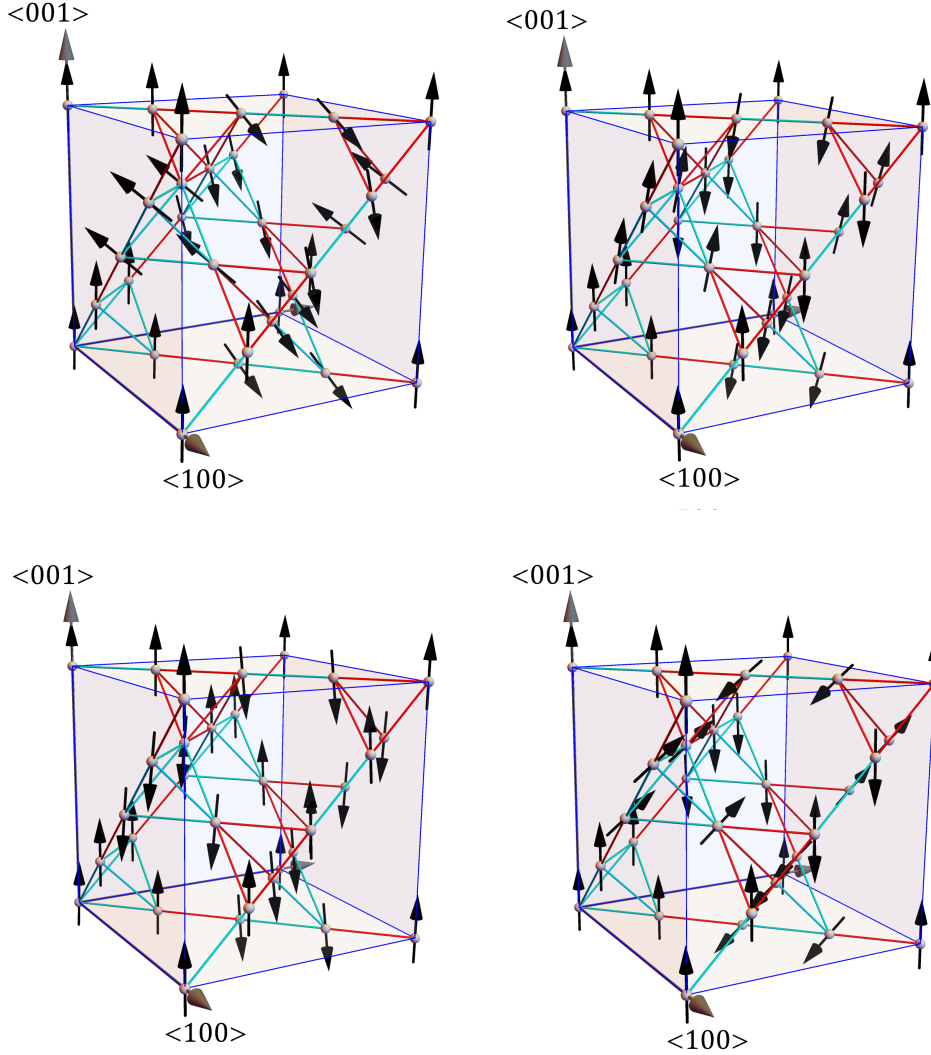


Figure 4.16: Four cubic supercells from four different $16 \times 16 \times 16$ unit cell systems from CMC simulations of the up-to-5th-NN model. Each cubic cell is from a different system thermalized at $0.02 \text{ K} \sim 10^{-3} T_C$. Notice how all the spins along the corners of the cubes point in the same direction (up). This suggests that the states are at ordering wavevectors $\mathbf{Q} = \frac{2\pi}{a}(\pm 1, 0, 0)$ or $\mathbf{Q} = \frac{2\pi}{a}(\pm 1, \pm 1, 0)$, with the cubic supercells being repeating units.

Comparison with Large- N and MFT

The results from Monte Carlo mean that below the critical temperature, one should expect Bragg peaks at $\mathbf{Q} = \frac{2\pi}{a}(\pm 1, 0, 0)$ and $\mathbf{Q} = \frac{2\pi}{a}(\pm 1, \pm 1, 0)$. The results from Monte Carlo when using the up-to-5th-NN parameters agree with large- N by virtue of the ordering wavevectors being discrete. The results for the up-to-3rd-NN parameters, however, differ between Monte Carlo and large- N . While large- N predicted the system with up-to-3rd-NN parameters to have intensity along the outline of the box with corners $\mathbf{Q} = \frac{2\pi}{a}(\pm 1, \pm 1, 0)$ with smooth modulation along the box's edges, Monte Carlo simulations predict Bragg peaks at the midpoint of the box edges and the corners. Comparing the altered up-to-3rd-NN parameters between Monte Carlo and large- N , as done in Figs. 4.11-4.14 also shows some differences in the ordering wavevector, suggesting that there are selection mechanisms for the ordering wavevectors in Monte Carlo that large- N fails to predict.

Model	T_C^{MF} (K)	$T_C^{\text{CMC}}(K)$	Θ_{CW}
Up to 3 rd NN	20.475	9.9(1)	-37.125
Up to 5 th NN	33.75	21.6(1)	-41.85

Table 4.1: Table containing the mean-field critical temperature, T_C^{MF} , the classical Monte Carlo critical temperature, T_C^{CMC} , and the Curie-Weiss temperature, Θ_{CW} . These temperatures are shown for both the up-to-3rd-NN and up-to-5th-NN models, whose exchange couplings are given in Table 3.1.

4.5 Chapter Summary

In this chapter, we showed results from numerical Monte Carlo simulations. For both the up-to-3rd-NN and the up-to-5th-NN models, the Monte Carlo simulations at low temperatures lead the systems to order at the commensurate wavevectors $\mathbf{Q} = 2\pi/a(\pm 1, 0, 0)$ or $\mathbf{Q} = 2\pi/a(\pm 1, \pm 1, 0)$. In contrast with large- N and MFT, where the up-to-3rd-NN model's structure factor forms peaks along the degeneracy lines, the up-to-3rd-NN model in Monte Carlo simulations gives Bragg peaks that sharpen with increasing system size. Similarly to large- N , the up-to-3rd-NN model is sensitive to alteration of the exchange parameters, which lead to changes for the ordering wavevectors. The Monte Carlo results for the up-to-5th-NN model show a critical temperature at around 20 K, similar to the experimental value, while the up-to-3rd-NN model's critical temperature in Monte Carlo simulations is lower, at ≈ 10 K.

Chapter 5

Discussion

5.1 Summary of Research

5.1.1 Monte Carlo versus Semi-Analytical

For this subsection, assume that the model being discussed is the up-to-3rd-NN Heisenberg model.

MFT and large- N give structure factors with high intensities throughout the degeneracy lines $\mathbf{Q} = 2\pi/a(\pm 1, h, 0)$ for a real number h , up to permutations of the coordinates. For the antiferromagnetic nearest-neighbour Heisenberg model on the FCC lattice (which has the same degeneracy lines of ordering wavevectors as the up-to-3rd-NN model), the structure factors from MFT and large- N have shown to be uniform along the degeneracy line. The reason for MFT and large- N giving structure factors that vary along the degeneracy line is due to the form factor of the lattice's basis, where the structure factor depends on the tetrahedral unit cell's wavevector-dependent form factor. Due to the variations of the form factors, the MFT and large- N structure factors form peaks along $\mathbf{Q} = 2\pi/a(\pm 1, 0, 0)$, with continuous modulation away from the peak along the line $\mathbf{Q} = 2\pi/a(\pm 1, h, 0)$. These peaks are not singular Bragg peaks since they are not isolated from the high-intensity region that form along the degeneracy line. In the quantum methods (PFFRG) and (PM-FRG), the structure factors also displays intensities along the degeneracy lines rather than singular peaks, although the modulation of the structure factor along the degeneracy lines is different and will be discussed in Section 5.1.2.

The specific heat and susceptibility from large- N agree with Monte Carlo simulations at high temperatures ($T \sim 100 \text{ K} \sim 10T_C$ for T_C obtained from CMC simulations), but

disagree at low temperatures ($T \sim 10 \text{ K} \sim T_C$). The disagreements could be in part due to approximations made by large- N . While the heat capacity and susceptibility were not computed for MFT in this thesis due to time limitations, MFT is expected to deviate from Monte Carlo as well due to approximations in MFT.

While the classical semi-analytical methods (MFT and large- N) and the quantum semi-analytical methods (PFFRG and PMFRG) show that the highest intensities of the structure factor are along the outline of the box with the corners $\mathbf{Q} = \frac{2\pi}{a}(\pm 1, \pm 1, 0)$ up to permutation of the Cartesian coordinates, classical Monte Carlo (CMC) simulations suggest that there are discrete Bragg peaks at $\mathbf{Q} = \frac{2\pi}{a}(\pm 1, \pm 1, 0)$ and $\mathbf{Q} = \frac{2\pi}{a}(\pm 1, 0, 0)$, up to permutations of the Cartesian coordinates. Out of the theoretical methods shown in the thesis, only classical Monte Carlo (CMC) gives Bragg peaks for the up-to-3rd-NN model. The reason for the peaks may be due to order by disorder (ObD), as illustrated in Fig. 5.1. The argument for the Bragg peaks seen in CMC simulations is order by disorder, since they are attained within the ground state manifold at states that permit the most modes of fluctuations. Indeed, the wavevectors of the Bragg peaks in the CMC structure factors are at $\mathbf{Q} = 2\pi/a(\pm 1, 0, 0)$ and $\mathbf{Q} = 2\pi/a(\pm 1, \pm 1, 0)$, which are intersection points of the ground state degeneracy lines. The intersections of degeneracy lines have more accessible modes of fluctuations within the ground-state manifold than any other wavevectors, and thus are selected by thermal order by disorder at low (but nonzero) temperatures.

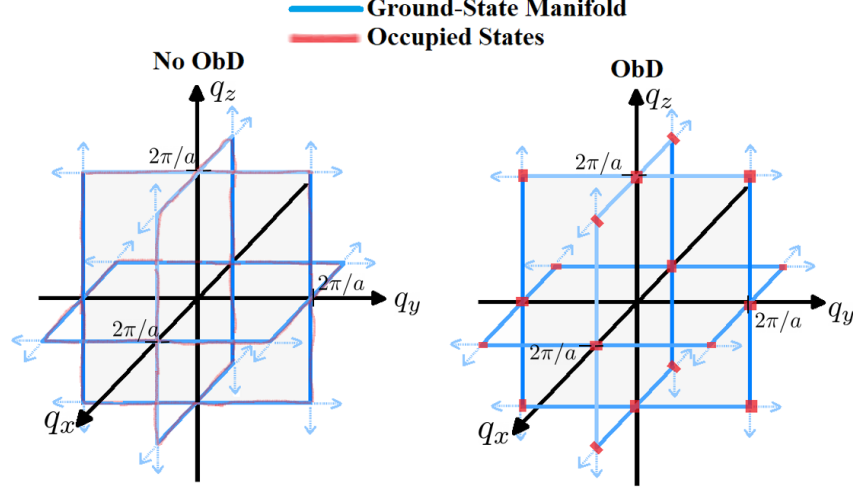


Figure 5.1: Illustration of order-by-disorder within the degeneracy lines that form the ground state manifold in the model using the up-to-3rd-NN couplings from density-functional theory (DFT). Although a ground state could be represented by any wavevector in the ground-state manifold, thermal fluctuations favour selection within the intersections of the degeneracy line. This order-by-disorder (ObD) selection within the ground state manifold favours states that permit more modes of thermal fluctuations for systems with nonzero temperatures [3].

5.1.2 Classical versus Quantum Semi-Analytical Methods

Since the quantum methods so far have been applied solely for the up-to-3rd-NN model, the classical methods for comparisons in this subsection are assumed to be for the up-to-3rd-NN model rather than the up-to-5th-NN model. While large- N and the quantum methods from our collaborators (PFFRG and PMFRG) give modulations along the degeneracy lines rather than Bragg peaks, the modulation in the quantum method is different from the modulation seen in the classical semi-analytical methods. The modulation in large- N and MFT peaks at the midpoint of the box edges, at wavevectors $2\pi/a(\pm 1, 0, 0)$ up to permutations of the coordinates. On the other hand, the peaks in PFFRG and PMFRG are away from the midpoint of the box edges, at $2\pi/a(\pm 1, \pm q, 0)$ up to permutations of the coordinates, for some temperature-dependent q . The disagreements in the location in the peak of the structure factor could be due to quantum effects that are captured by our collaborators' PFFRG and PMFRG but not captured in individual's classical methods. The deviation of the quantum methods' structure factor maxima away from the classical

methods' peaks could be due to quantum $1/S$ corrections [95]. A possible a method for linking the classical methods' results with our collaborators' quantum methods, high-temperature series expansion, will be discussed as a future plan in Section 5.2.

5.1.3 Theoretical versus Experimental Data

The remaining question is how the theoretical results from the various methods compare with the existing experimental data. Since our collaborators' experimental neutron scattering data is from $\text{CuAlCr}_4\text{S}_8$ powder samples rather than a single crystal, the moduli of the wavevectors at Bragg peaks are known, but the exact wavevectors are not.

The peaks in the experimental powder average do not correspond to any of the peaks predicted by the classical methods, but were compared with peaks of the form $\mathbf{Q} = (\pm 2\pi/a, q_k, 0)$ seen in PFFRG and PMFRG to give a possible fit for some of the experimental peaks when assuming $q_k \approx 0.07\text{\AA}$, as can be seen in Fig. 5.2a).

For the up-to-3rd-NN model with exchange couplings from DFT, the theoretical results disagree with the experimental data. This is so because the experimental data shows a Bragg peak that corresponds to a wavevector with a modulus $\approx 0.57\text{\AA}$, which is too low to be any theoretically predicted ordering wavevector in our model. To address disagreements among theoretical methods and experimental data, the classical methods were investigated for up-to-3rd-NN couplings that were altered from the values provided by DFT. This alteration was done to check the sensitivity of the theoretical model to perturbations. The alteration shows that the ground-state degeneracy can be broken by perturbations of the up-to-3rd-NN couplings. This results in peaks in the structure factor of the form $(\pm q_h, \pm q_h, 0) + \mathbf{G}$ where q_h depends on the altered exchange couplings. Furthermore, these alterations also showed that it is possible to perturb the Hamiltonian into q_h values that lead to a Bragg peaks with a modulus that is low enough to coincide with the lowest-momentum experimental peak. The experimental powder average data from our collaborators was compared with types of ordering wavevectors that appeared when altering the original up-to-3rd-NN couplings from DFT, which have the form $(\pm q_h, \pm q_h, 0) + \mathbf{G}$ for reciprocal lattice $\mathbf{G}$. The peaks of the form $(\pm 0.402, \pm 4.02, 0)\text{\AA} + \mathbf{G}$ agree with some of the magnetic peaks in the experimental data, as can be in Fig. 5.2b).

Although Fig. 5.2b) attempts to match the experimental peaks with candidate theoretical peaks of the form $(\pm q_h, \pm q_h, 0) + \mathbf{G}$, this candidate theoretical peaks only appear for variations of the exchange couplings in the up-to-3rd-NN model, and not necessarily for variations of the up-to-5th-NN model. While the ordering wavevectors in the 3rd-NN model are sensitive to alteration of the exchange couplings (as seen in the phase diagram in

Fig. 3.15), the up-to-5th-NN model is not as sensitive to alterations of its couplings, with the ordering wavevectors remaining at $\mathbf{Q} = 2\pi/a(\pm 1, 0, 0)$ and $\mathbf{Q} = 2\pi/a(\pm 1, \pm 1, 0)$ unless the alterations to the exchange couplings are drastic (such as $\sim 100\%$ changes to the dominant couplings' values).

Moreover, the candidate theoretical peaks, which are marked as the vertical dashed lines in Fig. 5.2, are chosen by fixing the values of parameter q_k in $2\pi/a(1, q_k, 0)$ in Fig. 5.2a) or the parameter q_h in $(q_h, q_h, 0)$ in Fig. 5.2b). The parameters' fixed values are chosen to give the best agreement with experimental results, but even then, these choices of parameters fail to predict some experimental peaks while predicting peaks where the experimental data observes none. For this reason, finding the ordering wavevectors corresponding to the experimental Bragg peaks is an ongoing research.

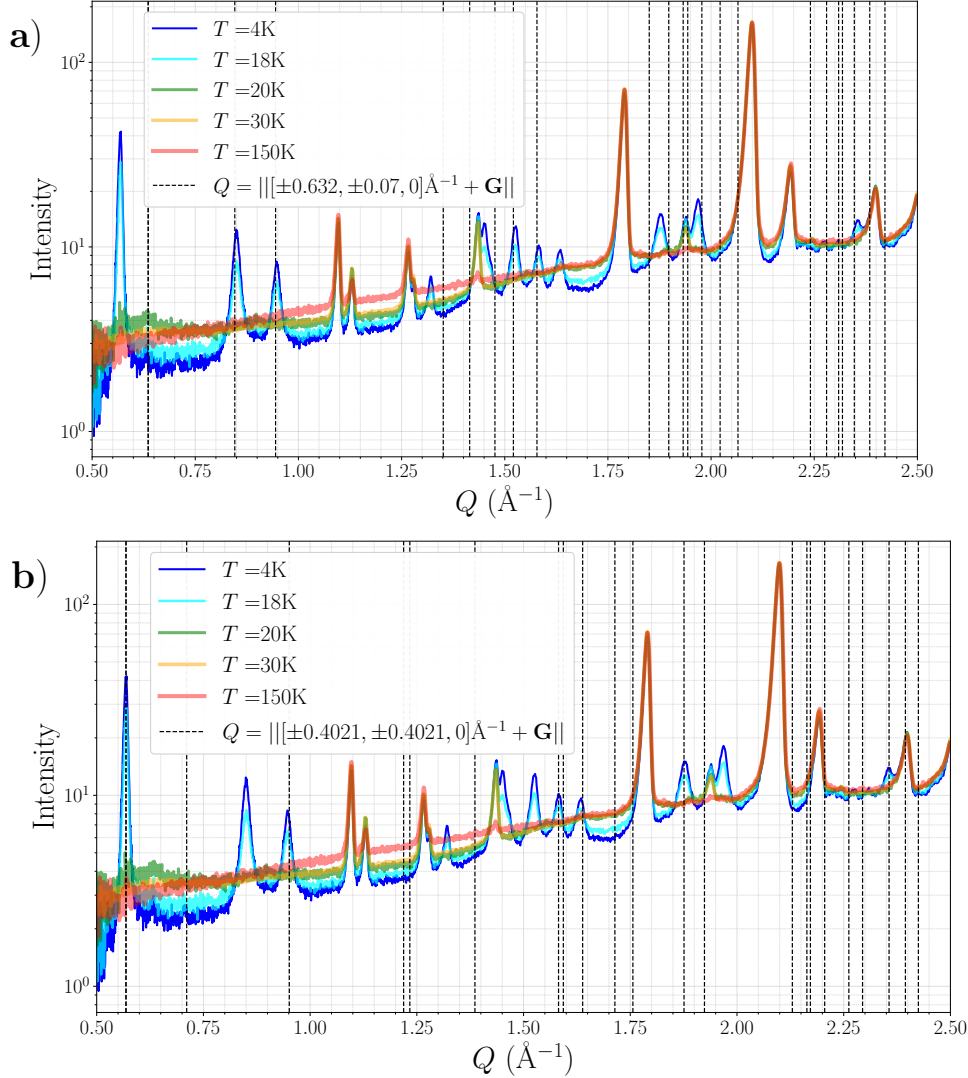


Figure 5.2: [Data included with permission from Sudarshan Sharma, McMaster University] Plots of experimental neutron scattering powder average for $\text{CuAlCr}_4\text{S}_8$. The peaks of interest are the blue peaks, which only appear below the critical temperature due to magnetic ordering. **a)** Experimental powder average compared with vertical dashed lines at the expected locations of peaks of the form $[hh0] + \mathbf{G}$, which are types of peaks seen when altering the exchange parameters in the up-to-3rd-NN model. **b)** Same experimental data, with vertical dashed line at peaks of the form $2\pi/a(1, q_k, 0) + \mathbf{G}$, which are the types of peaks seen in our collaborators' PFFRG and PMFRG.

5.1.4 Insight on Current Results

We have compared the results from the numerical CMC simulations with the results from semi-analytical methods in Section. 5.1.1. In that comparison, CMC shows Bragg peaks in the structure factor while none of the semi-analytical methods do. We have also compared results from classical methods with results from quantum methods in Section. 5.1.2. In that comparison, the classical methods give maxima in structure factor at commensurate wavevectors, while the quantum methods give maxima in the structure factor at potentially incommensurate wavevectors (according to current sampling resolution).

The disagreements among the methods when using the unaltered up-to-3rd-NN DFT couplings have cast doubts on the reliability of truncating exchange couplings beyond 3rd-NN. These doubts are intensified when considering the sensitivity of the up-to-3rd-NN Hamiltonian to perturbations. Another reason to question the truncation at the 3rd-NN couplings is that the 3rd-NN couplings in the up-to-3rd-NN model are stronger than any of the nearer-neighbour couplings. This suggests that there could be interactions beyond 3rd-NN that are significant. To address these doubts, the DFT data from our collaborators was updated to an Heisenberg model with exchange couplings up to 5th NN, which showed a significant 4th-NN coupling at $\approx 1\text{K}$ (for reference, the strongest coupling is $J_{3a} \approx 6\text{ K}$ for the up-to-5th NN models). From CMC simulations, this updated set of couplings gives a critical temperature that is closer to the experimental critical temperature of $\text{CuAlCr}_4\text{S}_8$. Moreover, the 4th and 5th NN couplings break the degeneracy in the global minimum of the classical energy bands (as seen when comparing Fig. 3.2 with Fig. 3.3). However, the global minimum in the classical up-to-5th-NN model suggests that the ordering wavevectors should be the commensurate $2\pi/a(\pm 1, 0, 0)$ or $2\pi/a(\pm 1, \pm 1, 0)$. While these ordering wavevectors were also the results from classical methods with up-to-3rd-NN coupling, the up-to-5th-NN model has these wavevectors selected as discrete ground states rather than having a degeneracy line of ordering wavevectors. The classical result for the ordering wavevectors in the up-to-5th-NN model disagrees with the experimental powder-average data. While perturbations of the up-to-3rd-NN coupling alters the ordering wavevector obtained by classical methods, alterations to the up-to-5th-NN couplings does not have the same impact on the ordering wavevectors; the commensurate peaks in the up-to-5th-NN model are unaltered unless the exchange couplings are changed into values way beyond their range of uncertainty. While the up-to-5th-NN has been expected to improve the predictions with experiment, and CMC simulations of the model does provide a closer critical temperature to the experimental value, there are still stark disagreements between the ordering wavevectors predicted by theoretical up-to-5th-NN model and the Bragg peaks in the experimental powder average data. The up-to-5th-NN model has not yet been ruled

out for its ability to describe experiments, as the disagreements between the classical theoretical methods and experiments may be due to the classical methods' lack of quantum contributions. At the time of writing, the up-to-5th-NN model has yet to be investigated by our collaborators' quantum methods, PFFRG and PMFRG. If the quantum methods for the up-to-5th-NN model will still disagree with the experimental Bragg peaks, then it could be that the interaction parameters in the models used are inaccurate. In that case, alternative methods to model the system will be needed, which are discussed in Section 5.2.

5.2 Outlook for Future Research

There is still a question on whether $\text{CuAlCr}_4\text{S}_8$ can be represented as a Heisenberg model with up-to-5th-NN couplings, or whether there are significant further-neighbour couplings. The DFT that goes up to 5th-NN couplings not only gives non-zero couplings to the newly added further-neighbour interactions (J_4 and J_5), but also renormalizes the values for pre-existing closer-range exchange couplings. Some are updated slightly, while others, such as J_{1a} change significantly (from -0.2 K to 2 K). While we addressed the question of whether the up-to-3rd-NN model has a sufficient interaction range, the same question still applies to the up-to- 5th-NN model. The significant change for some of the exchange parameters when updating the up-to-3rd-NN model to up-to- 5th-NN begs the question of whether stopping at 5th-NN couplings is sufficient. Ideally, once adding any new further-neighbour interaction gives significantly weaker interaction strengths for the furthest neighbours without renormalizing the nearer neighbours, then this would reassure that the interaction ranges considered go far enough to represent the system accurately.

The outstanding question is how the system orders and why. The differences among the quantum PFFRG/PMFRG methods, Large- N , and Monte Carlo pose questions regarding the ordering wavevectors. The disagreements between quantum and classical methods could be addressed by performing high-temperature series expansion [96], which could be compared with our collaborators' PMFRG method at high temperatures. Disagreements between experimental data and theoretical methods prompt us to consider whether the model obtained by DFT is sufficiently accurate. Another method to obtain exchange couplings is by fitting to experimental data, which has been compared with DFT for some other chromium spinel, $\text{LiGaCr}_4\text{S}_8$ [63]. For $\text{LiGaCr}_4\text{S}_8$, while an up-to-3rd-NN Heisenberg model with parameters from DFT has shown some fair agreement with experimental data, the model has shown a significantly better agreement with experimental data when using Heisenberg interaction parameters from fitting to experimental data. The results

for $\text{LiGaCr}_4\text{S}_8$ are an incentive for extracting Heisenberg coupling values from fitting to experimental data of $\text{CuAlCr}_4\text{S}_8$.

To understand the models better, it may be beneficial to analyze the theoretical models with different approaches. A possible approach could be to analyze the behaviour of $\text{CuAlCr}_4\text{S}_8$ by perturbing four weakly-interacting FCC lattices. For example, one could expand on the effective FCC model, which is applicable for $\text{CuAlCr}_4\text{S}_8$ since the exchange couplings in $\text{CuAlCr}_4\text{S}_8$ show strongest couplings between neighbours related by primitive FCC translations. Since the FCC model is simpler than the breathing pyrochlore by virtue of being a Bravais lattice, analytical perturbations on the model could give insight on the behaviour of the ordering wavevectors. Another approach could be to carry out mathematical analyses of entropy at low temperatures. This mathematical analysis could give insight on the thermal order-by-disorder that is suggested in CMC simulations for the up-to-3rd-NN model.

While currently the experimental data on neutron scattering is limited to powder average, it is still possible to infer ordering wavevector(s) due to the fact that for every peak seen in a wavevector $\|\mathbf{q}_{\text{ord}}\|$ there should be peaks at $\|\mathbf{q}_{\text{ord}} + \mathbf{G}\|$ for reciprocal lattice vectors $\mathbf{G}$. This method was used successfully before for the complex $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ frustrated garnet [97]. The possibility of inferring ordering wavevectors from powder average, however, becomes difficult when there are multiple ordering wavevectors within the Brillouin zone, which has been theorized to be possible in the chromium spinel $\text{CuInCr}_4\text{S}_8$ (which is closely related to but should not to be confused with the titular $\text{CuAlCr}_4\text{S}_8$) [98].

If extracting the ordering wavevectors from experimental data for comparison with theoretical methods is not feasible, there are other possibilities for comparisons of spin-spin correlations. For example, while our research focused on finding the ordering wavevector, it remains to compare diffuse scattering among the theoretical methods and experimental data. Diffuse scattering refers to the broadening of structure factor peaks as the temperature increases, and its analysis can be performed at temperatures above the critical temperatures [99]. The temperature-dependent evolution of experimental diffuse scattering data can be used to compare with theoretical models or to construct a best-fit theoretical model by methods such as reverse Monte Carlo (RMC).

5.3 Conclusion

There are multiple methods used to model $\text{CuAlCr}_4\text{S}_8$ as well as experimental data, with conflicting results for the ordering wavevectors of the spins. For both the up-to-3rd-NN and

up-to-5th-NN couplings, classical Monte Carlo suggests that there are ordering wavevectors of the forms $2\pi/a(\pm 1, 0, 0)$ and $2\pi/a(\pm 1, \pm 1, 0)$, up to permutations of the coordinates. For the up-to-3rd-NN couplings, MFT and large- N suggest high-intensity structure factors along the ground-state degeneracy lines, which form the outline of the box with corners at $2\pi/a(\pm 1, \pm 1, 0)$. Within the high intensity of the degeneracy lines, there is modulation in the structure factor that maximizes the structure factors for MFT and large- N at the midpoints of the box edges, $2\pi/a(\pm 1, 0, 0)$, due to the tetrahedral unit cell's wavevector-dependent form factors. For the up-to-5th-NN couplings, MFT and large- N have Bragg peaks at the same wavevectors as CMC simulations do. In the case of the up-to-3rd-NN model, only CMC simulations give discrete ordering wavevectors out of the classical methods, and this ordering breaks the accidental degeneracy in the ground state manifold, suggesting order by disorder [28, 100]. Biquadratic interactions were not ruled out as a possible contribution to the Hamiltonian. Due to the quartic order of biquadratic interactions, if quartic interactions are non-negligible, they could render methods that rely on Gaussian approximations like large- N and MFT unusable. If biquadratic interactions are to be included in the model, then they would be possible to incorporate into CMC. Biquadratic spin interactions might arise due to quartic-order spin terms from super-exchange interactions between spins with $S > 1/2$. They may also arise due to deformations of the lattice at low temperatures. Moreover, biquadratic interactions may arise due to dynamical lattice fluctuations [40, 50, 101–103]. Although the nature of biquadratic corrections due to the super-exchange interactions or due to dynamical fluctuations in $\text{CuAlCr}_4\text{S}_8$ has yet to be explored, our collaborators' most recent experimental data suggests that it is safe to rule out low-temperature lattice deformation in $\text{CuAlCr}_4\text{S}_8$. This is so since no significant lattice deformations were observed by our collaborating experimentalists for temperatures between 10 K and room temperature, suggesting that the phase transition at $T \approx 20$ K is magnetic and not due to structural deformations. Besides ruling out lattice deformation as a possible cause for biquadratic interactions, lattice deformation has also been ruled out as a possible cause for the phase transition.

To summarize the whole thesis' work and our collaborators' work so far, whether the classical theoretical methods fail to predict the ordering wavevector(s) of spins in $\text{CuAlCr}_4\text{S}_8$ due to neglecting quantum fluctuations or due to missing terms in the Hamiltonian, the reason for the disagreements is an ongoing question.

References

- [1] M. Gen, H. Ishikawa, A. Miyake, T. Yajima, H. O. Jeschke, H. Sagayama, A. Ikeda, Y. H. Matsuda, K. Kindo, M. Tokunaga, Y. Kohama, T. Kurumaji, Y. Tokunaga, and T. Arima, “Breathing pyrochlore magnet $\text{CuGaCr}_4\text{S}_8$: Magnetic, thermodynamic, and dielectric properties,” [arXiv:2303.10671 \(2023\)](#).
- [2] R. G. Bowers and M. E. Woolf, “Some critical properties of the heisenberg model,” [Phys. Rev. **177**, 917–932 \(1969\)](#).
- [3] R. Schick, T. Ziman, and M. E. Zhitomirsky, “Quantum versus thermal fluctuations in the fcc antiferromagnet: Alternative routes to order by disorder,” [Phys. Rev. B **102**, 220405 \(2020\)](#).
- [4] P. Ghosh, Y. Iqbal, T. Müller, R. T. Ponnaganti, R. Thomale, R. Narayanan, J. Reuther, M. J. P. Gingras, and H. O. Jeschke, “Breathing chromium spinels: a showcase for a variety of pyrochlore Heisenberg Hamiltonians,” [npj Quantum Materials **4**, 63 \(2019\)](#).
- [5] T. Vicsek, A. Czirók, E. Ben-Jacob, I. Cohen, and O. Shochet, “Novel Type of Phase Transition in a System of Self-Driven Particles,” [Phys. Rev. Lett. **75**, 1226-1229 \(1995\)](#).
- [6] D. Christian, “The idea of emergence,” in *This Explains Everything*, J. Brockman, Ed. New York, NY: HarperPerennial, Jan. 2013.
- [7] R. K. Pathria and P. D. Beale, *Statistical mechanics*, 3rd ed. Amsterdam ; Boston: Elsevier/Academic Press, 2011.
- [8] E. Du Trémolet de Lacheisserie, D. Gignoux, and M. Schlenker, *Magnetism. Fundamentals*. New York: Springer Science+Business Media New York, 2005.
- [9] J. C. Slater, “The ferromagnetism of nickel,” [Phys. Rev. **49**, 537 \(1936\)](#).

- [10] C. Lacroix, P. Mendels, and F. Mila, Eds., *Introduction to Frustrated Magnetism: Materials, Experiments, Theory*, ser. Springer Series in Solid-State Sciences. Berlin, Heidelberg: Springer Berlin Heidelberg, [164 \(2011\)](#).
- [11] S. R. A. Salinas, *Introduction to Statistical Physics*, ser. Graduate Texts in Contemporary Physics, R. S. Berry, J. L. Birman, J. W. Lynn, M. P. Silverman, H. E. Stanley, and M. Voloshin, Eds., New York, NY, [Springer New York, \(2001\)](#).
- [12] W. Lenz, “Beitrag zum verständnis der magnetischen erscheinungen in festen körpern,” pp. 613–615, 1924.
- [13] E. Ising, “Beitrag zur theorie des ferromagnetismus,” [Zeitschrift für Physik **31**, 253–258 \(1925\)](#).
- [14] L. Onsager, “Crystal Statistics. I. A Two-Dimensional Model with an Order-Disorder Transition,” [Phys. Rev. **65**, 117–149 \(1944\)](#).
- [15] L. Néel, “Antiferromagnetism and ferrimagnetism,” [Proc. Phys. Soc. **65**, 869 \(1952\)](#).
- [16] J. S. Gardner, M. J. P. Gingras, and J. E. Greedan, “Magnetic pyrochlore oxides,” [Rev. Mod. Phys. **82**, 53–107 \(2010\)](#).
- [17] J. Vannimenus and G. Toulouse, “Theory of the frustration effect. II. Ising spins on a square lattice,” [J. Phys. C: Solid State Phys. **10**, L537–L542 \(1977\)](#).
- [18] J. Villain, “Insulating spin glasses,” [Zeitschrift für Physik B Condensed Matter **33**, 31–42 \(1979\)](#).
- [19] G. H. Wannier, “Antiferromagnetism. The Triangular Ising Net,” [Phys. Rev. **79**, 357–364 \(1950\)](#).
- [20] R. M. F. Houtappel, *Order-Disorder in Hexagonal Lattices*. Dordrecht: Springer Netherlands, [pp. 1–31 \(1950\)](#).
- [21] M. J. Harris, S. T. Bramwell, D. F. McMorrow, T. Zeiske, and K. W. Godfrey, “Geometrical Frustration in the Ferromagnetic Pyrochlore $\text{Ho}_2\text{Ti}_2\text{O}_7$,” [Phys. Rev. Lett. **79**, 2554–2557 \(1997\)](#).
- [22] R. Moessner, “Magnets with strong geometric frustration,” [Canadian Journal of Physics **79**, 1283–1294 \(2001\)](#).

- [23] L. Pauling, “The Structure and Entropy of Ice and of Other Crystals with Some Randomness of Atomic Arrangement,” *Journal of the American Chemical Society*, [Journal of the American Chemical Society](#) **57**, 2680–2684 (1935).
- [24] —, *The nature of the chemical bond*. George Banta Co., 1960.
- [25] P. Anderson, “Resonating valence bonds: A new kind of insulator?” [Materials Research Bulletin](#) **8**, 153–160 (1973).
- [26] D. Bergman, J. Alicea, E. Gull, S. Trebst, and L. Balents, “Order by disorder and spiral spin liquid in frustrated diamond lattice antiferromagnets,” [Nature Physics](#) **3**, 487–491 (2007).
- [27] R. Moessner and J. T. Chalker, “Low-temperature properties of classical geometrically frustrated antiferromagnets,” [Phys. Rev. B](#) **58**, 12049 (1998).
- [28] S. Khatua, M. J. P. Gingras, and J. G. Rau, “Pseudo-goldstone modes and dynamical gap generation from order by thermal disorder,” [Phys. Rev. Lett.](#) **130**, 266702 (2023).
- [29] L. Savary, K. A. Ross, B. D. Gaulin, J. P. C. Ruff, and L. Balents, “Order by quantum disorder in $\text{Er}_2\text{Ti}_2\text{O}_7$,” [Phys. Rev. Lett.](#) **109**, 167201 (2012).
- [30] C. Kittel, *Introduction to solid state physics*, 8th ed. Hoboken, NJ: Wiley, 2005.
- [31] I. A. Assi and S. H. Curnoe, “Analytic description of spin waves in dipolar/octupolar pyrochlore magnets,” [Journal of Physics: Condensed Matter](#) **33**, 165802 (2021).
- [32] S. Dissanayake, Z. Shi, J. G. Rau, R. Bag, W. Steinhardt, N. P. Butch, M. Frontzek, A. Podlesnyak, D. Graf, C. Marjerrison, J. Liu, M. J. P. Gingras, and S. Haravifard, “Towards understanding the magnetic properties of the breathing pyrochlore compound $\text{Ba}_3\text{Yb}_2\text{Zn}_5\text{O}_{11}$ through single-crystal studies,” [npj Quantum Materials](#) **7**, 77 (2022).
- [33] S. Sharma, M. Pocrnic, B. N. Riechert, C. R. Wiebe, J. Beare, J. Gautreau, J. P. Clancy, J. P. C. Ruff, M. Pula, Q. Chen, S. Yoon, Y. Cai, and G. M. Luke, “Synthesis and physical and magnetic properties of $\text{CuAlCr}_4\text{S}_8$: A Cr-based breathing pyrochlore,” [Phys. Rev. B](#), **106**, 024407 (2022).
- [34] H. Pinch, M. Woods, and E. Lopatin, “Some new mixed A-site chromium chalcogenide spinels,” [Materials Research Bulletin](#) **5**, 425–429 (1970).

- [35] Z. He, Y. Gu, H. Wo, Y. Feng, D. Hu, Y. Hao, Y. Gu, H. C. Walker, D. T. Adroja, and J. Zhao, “Neutron Scattering Studies of the Breathing Pyrochlore Antiferromagnet $\text{LiGaCr}_4\text{O}_8$,” *Phys. Rev. Lett.*, **127**, 147205 (2021).
- [36] J. G. Rau, L. S. Wu, A. F. May, A. E. Taylor, I.-L. Liu, J. Higgins, N. P. Butch, K. A. Ross, H. S. Nair, M. D. Lumsden, M. J. P. Gingras, and A. D. Christianson, “Behavior of the breathing pyrochlore lattice $\text{Ba}_3\text{Yb}_2\text{Zn}_5\text{O}_{11}$ in applied magnetic field,” *Journal of Physics: Condensed Matter* **30**, 455801 (2018).
- [37] J. G. Rau, L. S. Wu, A. F. May, L. Poudel, B. Winn, V. O. Garlea, A. Huq, P. Whitfield, A. E. Taylor, M. D. Lumsden, M. J. P. Gingras, and A. D. Christianson, “Anisotropic exchange within decoupled tetrahedra in the quantum breathing pyrochlore $\text{Ba}_3\text{Yb}_2\text{Zn}_5\text{O}_{11}$,” *Phys. Rev. Lett.* **116**, 257204 (2016).
- [38] J. G. Rau and M. J. Gingras, “Frustrated Quantum Rare-Earth Pyrochlores,” *Annual Review of Condensed Matter Physics* **10**, 357–386 (2019).
- [39] P. Fazekas, *Lecture notes on electron correlation and magnetism*. World Scientific, 1999, vol. 5.
- [40] J. G. Rau, L. S. Wu, A. F. May, L. Poudel, B. Winn, V. O. Garlea, A. Huq, P. Whitfield, A. E. Taylor, M. D. Lumsden, M. J. P. Gingras, and A. D. Christianson, “Anisotropic Exchange within Decoupled Tetrahedra in the Quantum Breathing Pyrochlore $\text{Ba}_3\text{Yb}_2\text{Zn}_5\text{O}_{11}$,” *Phys. Rev. Lett.* **116**, 257204 (2016).
- [41] E. Coronado, P. Delhaès, D. Gatteschi, and J. S. Miller, *Molecular Magnetism: From Molecular Assemblies to the Devices*, Dordrecht: Springer Netherlands, 1996.
- [42] S. Keshavarz, J. Schött, A. J. Millis, and Y. O. Kvashnin, “Electronic structure, magnetism, and exchange integrals in transition-metal oxides: Role of the spin polarization of the functional in DFT+ U calculations,” *Phys. Rev. B* **97**, 184404 (2018).
- [43] M. Elhajal, B. Canals, R. Sunyer, and C. Lacroix, “Ordering in the pyrochlore antiferromagnet due to Dzyaloshinsky-Moriya interactions,” *Physical Review B* **71**, 094420 (2005).
- [44] R. G. Burns, “Crystal field effects in chromium and its partitioning in the mantle,” *Geochimica et Cosmochimica Acta* **39**, 857–864 (1975).
- [45] N. W. Ashcroft and N. D. Mermin, *Solid state physics*. Harcourt College Publishers, 1976.

- [46] S. E. Palmer and J. T. Chalker, “Order induced by dipolar interactions in a geometrically frustrated antiferromagnet,” *Phys. Rev. B* **62**, 488–492 (2000).
- [47] B. C. den Hertog and M. J. P. Gingras, “Dipolar interactions and origin of spin ice in ising pyrochlore magnets,” *Phys. Rev. Lett.* **84**, 3430–3433 (2000).
- [48] P. K. Yadav, M. Tolkiehn, and C. Upadhyay, “Dielectric relaxations in $\text{Ho}_2\text{Ti}_2\text{O}_7$ and $\text{Dy}_2\text{Ti}_2\text{O}_7$ pyrochlores,” *Journal of Physics and Chemistry of Solids* **134**, 201–208 (2019).
- [49] M. J. Gingras and B. C. den Hertog, “Origin of spin-ice behavior in ising pyrochlore magnets with long-range dipole interactions: an insight from mean-field theory,” *Canadian Journal of Physics* **79**, 1339–1351 (2001).
- [50] O. Tchernyshyov, R. Moessner, and S. L. Sondhi, “Spin-Peierls phases in pyrochlore antiferromagnets,” *Phys. Rev. B* **66**, 064403 (2002).
- [51] A. Sadeghi, M. Alaei, F. Shahbazi, and M. J. P. Gingras, “Spin Hamiltonian, order out of a Coulomb phase, and pseudocriticality in the frustrated pyrochlore Heisenberg antiferromagnet FeF_3 ,” *Phys. Rev. B* **91**, 140407 (2015).
- [52] Y. Tanaka, M. Yoshida, M. Takigawa, Y. Okamoto, and Z. Hiroi, “Novel Phase Transitions in the Breathing Pyrochlore Lattice: ^7Li -NMR on $\text{LiInCr}_4\text{O}_8$ and $\text{LiGaCr}_4\text{O}_8$,” *Phys. Rev. Lett.* **113**, 227204 (2014).
- [53] K. Miyoshi, Y. Takaichi, Y. Takamatsu, M. Miura, and J. Takeuchi, “Superconducting Transition in the β -Pyrochlore AOs_2O_6 ($A = \text{Cs, Rb, K}$) under Pressure,” *Journal of the Physical Society of Japan* **77**, 043704 (2008).
- [54] S. Yonezawa, Y. Muraoka, Y. Matsushita, and Z. Hiroi, “Superconductivity in a pyrochlore-related oxide KOs_2O_6 ,” *Journal of Physics: Condensed Matter* **16**, L9–L12 (2004).
- [55] M. Brühwiler, S. M. Kazakov, N. D. Zhigadlo, J. Karpinski, and B. Batlogg, “Superconductivity in the geometrically frustrated pyrochlore RbOs_2O_6 ,” *Phys. Rev. B* **70**, 020503 (2004).
- [56] C. Wengel, C. L. Henley, and A. Zippelius, “Spin-glass and antiferromagnet critical behavior in a diluted fcc antiferromagnet,” *Phys. Rev. B* **53**, 6543–6553 (1996).
- [57] L. Savary, X. Wang, H.-Y. Kee, Y. B. Kim, Y. Yu, and G. Chen, “Quantum spin ice on the breathing pyrochlore lattice,” *Phys. Rev. B* **94**, 075146 (2016).

- [58] J. R. Chamorro, T. M. McQueen, and T. T. Tran, “Chemistry of Quantum Spin Liquids,” [Chem. Rev. **121**, 2898–2934 \(2021\)](#).
- [59] O. Benton, O. Sikora, and N. Shannon, “Seeing the light: Experimental signatures of emergent electromagnetism in a quantum spin ice,” [Phys. Rev. B **86**, 075154 \(2012\)](#).
- [60] E. Z. Zhang, F. L. Buessen, and Y. B. Kim, “Dynamical signatures of rank-2 $U(1)$ spin liquids,” [Phys. Rev. B **105**, L060408 \(2022\)](#).
- [61] M. Ezawa, “Higher-Order Topological Insulators and Semimetals on the Breathing Kagome and Pyrochlore Lattices,” [Phys. Rev. Lett. **120**, 026801 \(2018\)](#).
- [62] R. Wawrzyńczak, Y. Tanaka, M. Yoshida, Y. Okamoto, P. Manuel, N. Casati, Z. Hiroi, M. Takigawa, and G. J. Nilsen, “Classical Spin Nematic Transition in $\text{LiGa}_{0.95}\text{In}_{0.05}\text{Cr}_4\text{O}_8$,” [Phys. Rev. Lett. **119**, 087201 \(2017\)](#).
- [63] G. Pokharel, H. S. Arachchige, T. J. Williams, A. F. May, R. S. Fishman, G. Sala, S. Calder, G. Ehlers, D. S. Parker, T. Hong, A. Wildes, D. Mandrus, J. A. Paddison, and A. D. Christianson, “Cluster Frustration in the Breathing Pyrochlore Magnet $\text{LiGaCr}_4\text{S}_8$,” [Phys. Rev. Lett. **125**, 167201 \(2020\)](#).
- [64] G. Pokharel, A. F. May, D. S. Parker, S. Calder, G. Ehlers, A. Huq, S. A. J. Kimber, H. S. Arachchige, L. Poudel, M. A. McGuire, D. Mandrus, and A. D. Christianson, “Negative thermal expansion and magnetoelastic coupling in the breathing pyrochlore lattice material $\text{LiGaCr}_4\text{S}_8$,” [Phys. Rev. B **97**, 134117 \(2018\)](#).
- [65] F.-Y. Li, Y.-D. Li, Y. B. Kim, L. Balents, Y. Yu, and G. Chen, “Weyl magnons in breathing pyrochlore antiferromagnets,” [Nature Communications **7**, 12691 \(2016\)](#).
- [66] R. Saha, R. Dhanya, C. Bellin, K. Béneut, A. Bhattacharyya, A. Shukla, C. Narayana, E. Suard, J. Rodríguez-Carvajal, and A. Sundaresan, “Magnetostructural coupling and magnetodielectric effects in the A-site cation-ordered spinel $\text{LiFeCr}_4\text{O}_8$,” [Phys. Rev. B **96**, 214439 \(2017\)](#).
- [67] G. M. Kalvius, O. Hartmann, A. Krimmel, F. E. Wagner, R. Wäppling, V. Tsurkan, H.-A. Krug Von Nidda, and A. Loidl, “Spin-lattice instability in the chromium sulfur spinel $\text{Fe}_{0.5}\text{Cu}_{0.5}\text{Cr}_2\text{S}_4$,” [Journal of Physics: Condensed Matter **20**, 252204 \(2008\)](#).
- [68] Y. Okamoto, G. J. Nilsen, J. P. Attfield, and Z. Hiroi, “Breathing Pyrochlore Lattice Realized in A-Site Ordered Spinel Oxides $\text{LiGaCr}_4\text{O}_8$ and $\text{LiInCr}_4\text{O}_8$,” [Phys. Rev. Lett. **110**, 097203 \(2013\)](#).

- [69] Y. Okamoto, G. J. Nilsen, T. Nakazono, and Z. Hiroi, “Magnetic Phase Diagram of the Breathing Pyrochlore Antiferromagnet $\text{LiGa}_{1-x}\text{In}_x\text{Cr}_4\text{O}_8$,” [Journal of the Physical Society of Japan](#) **84**, 043707 (2015).
- [70] I. Kézsmárki, S. Bordács, P. Milde, E. Neuber, L. M. Eng, J. S. White, H. M. Rønnow, C. D. Dewhurst, M. Mochizuki, K. Yanai, H. Nakamura, D. Ehlers, V. Tsurkan, and A. Loidl, “Néel-type skyrmion lattice with confined orientation in the polar magnetic semiconductor GaV_4S_8 ,” [Nature Materials](#) **14**, 1116–1122 (2015).
- [71] Y. Tanaka, R. Wawrzyńczak, M. D. Le, T. Guidi, Y. Okamoto, T. Yajima, Z. Hiroi, M. Takigawa, and G. J. Nilsen, “Inelastic Neutron Scattering Study of the Spin Dynamics in the Breathing Pyrochlore System $\text{LiGa}_{0.95}\text{In}_{0.05}\text{Cr}_4\text{O}_8$,” [Journal of the Physical Society of Japan](#) **87**, 073710 (2018).
- [72] D. Reig-i Plessis and A. M. Hallas, “Frustrated magnetism in fluoride and chalcogenide pyrochlore lattice materials,” [Phys. Rev. Materials](#) **5**, 030301 (2021).
- [73] S. Lee, S.-H. Do, W. Lee, Y. S. Choi, J. Van Tol, A. P. Reyes, D. Gorbunov, W.-T. Chen, and K.-Y. Choi, “Dichotomy in temporal and thermal spin correlations observed in the breathing pyrochlore $\text{LiGa}_{1-x}\text{In}_x\text{Cr}_4\text{O}_8$,” [npj Quantum Materials](#) **6**, 47 (2021).
- [74] K. Essafi, L. D. C. Jaubert, and M. Udagawa, “Flat bands and Dirac cones in breathing lattices,” [J. Phys.: Condens. Matter](#) **29**, 315802 (2017).
- [75] A. Furrer, J. Mesot, and T. Straessle, *Neutron Scattering In Condensed Matter Physics*, ser. Series On Neutron Techniques And Applications, [World Scientific Publishing Company](#), 2009.
- [76] J. Jensen and A. R. Mackintosh, *Rare earth magnetism*. Oxford: Clarendon Press, 1991.
- [77] A. P. Murani, “Neutron scattering studies of spin-glass alloys,” [Journal of Applied Physics](#) **49**, 1604–1609 (1978).
- [78] K. T. K. Chung, J. S. K. Goh, A. Mukherjee, W. Jin, D. Lozano-Gómez, and M. J. P. Gingras, “Probing flat band physics in spin ice systems via polarized neutron scattering,” [Phys. Rev. Lett.](#) **128**, 107201 (2022).
- [79] A. P. Ramirez, “Strongly geometrically frustrated magnets,” [Annual Review of Materials Science](#) **24**, 453–480 (1994).

- [80] J. N. Reimers, A. J. Berlinsky, and A.-C. Shi, “Mean-field approach to magnetic ordering in highly frustrated pyrochlores,” [Phys. Rev. B **43**, 865–878 \(1991\)](#).
- [81] M. Enjalran and M. J. P. Gingras, “Theory of paramagnetic scattering in highly frustrated magnets with long-range dipole-dipole interactions: The case of the $\text{Tb}_2\text{Ti}_2\text{O}_7$, pyrochlore antiferromagnet,” [Phys. Rev. B **70**, 174426 \(2004\)](#).
- [82] J. N. Reimers, “Diffuse-magnetic-scattering calculations for frustrated antiferromagnets,” [Phys. Rev. B **46**, 193–202 \(1992\)](#).
- [83] P. H. Conlon and J. T. Chalker, “Absent pinch points and emergent clusters: further neighbour interactions in the pyrochlore Heisenberg antiferromagnet,” [Phys. Rev. B **81**, 224413 \(2010\)](#).
- [84] T. Mizoguchi, L. D. C. Jaubert, R. Moessner, and M. Udagawa, “Magnetic clustering, half-moons, and shadow pinch points as signals of a proximate coulomb phase in frustrated heisenberg magnets,” [Phys. Rev. B **98**, 144446 \(2018\)](#).
- [85] J. N. Reimers, “Absence of long-range order in a three-dimensional geometrically frustrated antiferromagnet,” [Phys. Rev. B **45**, 7287–7294 \(1992\)](#).
- [86] N. Rezaei, M. Alaei, and H. Akbarzadeh, “ESpinS: A program for classical Monte-Carlo simulations of spin systems,” [arXiv:1912.00793 \(2021\)](#).
- [87] J. D. Alzate-Cardona, D. Sabogal-Suárez, R. F. L. Evans, and E. Restrepo-Parra, “Optimal phase space sampling for monte carlo simulations of heisenberg spin systems,” [J. Phys.: Condens. Matter **31**, 095802 \(2019\)](#).
- [88] H. Dai, “A Review on the Exact Monte Carlo Simulation,” in *Bayesian Inference on Complicated Data*, N. Tang, Ed., [IntechOpen, \(2020\)](#).
- [89] M. Creutz, “Overrelaxation and Monte Carlo simulation,” [Phys. Rev. D **36**, 515–519 \(1987\)](#).
- [90] T. Müller, D. Kiese, N. Niggemann, B. Sbierski, J. Reuther, S. Trebst, R. Thomale, and Y. Iqbal, “Pseudo-fermion functional renormalization group for spin models,” [arXiv:2307.10359 \(2023\)](#).
- [91] J. Reuther and P. Wölfle, “A diagrammatic theory of the antiferromagnetic frustrated 2d Heisenberg model,” [J. Phys.: Conf. Ser. **200**, 022051 \(2010\)](#).

- [92] Y. Iqbal, T. Müller, P. Ghosh, M. J. P. Gingras, H. O. Jeschke, S. Rachel, J. Reuther, and R. Thomale, “Quantum and Classical Phases of the Pyrochlore Heisenberg Model with Competing Interactions,” [Phys. Rev. X **9**, 011005 \(2019\)](#).
- [93] N. Niggemann, B. Sbierski, and J. Reuther, “Frustrated Quantum Spins at finite Temperature: Pseudo-Majorana functional RG approach,” [Phys. Rev. B **103**, 104431 \(2021\)](#).
- [94] H. Hasegawa, “Wave vector-dependent spin susceptibility of iron above the curie temperature,” [J. Phys. F: Met. Phys. **13**, 2655 \(1983\)](#).
- [95] S.-L. Yu, W. Wang, Z.-Y. Dong, Z.-J. Yao, and J.-X. Li, “Deconfinement of spinons in frustrated spin systems: Spectral perspective,” [Phys. Rev. B **98**, 134410 \(2018\)](#).
- [96] A. Hehn, N. van Well, and M. Troyer, “High-temperature series expansion for spin-1/2 Heisenberg models,” [Computer Physics Communications, **212**, 180–188 \(2017\)](#).
- [97] T. Yavors’kii, M. Enjalran, and M. J. P. Gingras, “Spin Hamiltonian, Competing Small Energy Scales, and Incommensurate Long-Range Order in the Highly Frustrated $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ Garnet Antiferromagnet,” [Phys. Rev. Lett. **97**, 267203 \(2006\)](#).
- [98] M. Gen, H. Ishikawa, A. Ikeda, A. Miyake, Z. Yang, Y. Okamoto, M. Mori, K. Takenaka, H. Sagayama, T. Kurumaji, Y. Tokunaga, T. Arima, M. Tokunaga, K. Kindo, Y. H. Matsuda, and Y. Kohama, “Complex magnetic phase diagram with a small phase pocket in a three-dimensional frustrated magnet $\text{CuInCr}_4\text{S}_8$,” [Phys. Rev. Research **4**, 033148 \(2022\)](#).
- [99] G. J. Nilsen, C. M. Thompson, G. Ehlers, C. A. Marjerrison, and J. E. Greedan, “Diffuse magnetic neutron scattering in the highly frustrated double perovskite Ba_2YRuO_6 ,” [Phys. Rev. B **91**, 054415 \(2015\)](#).
- [100] J. T. Chalker, P. C. W. Holdsworth, and E. F. Shender, “Hidden order in a frustrated system: Properties of the Heisenberg Kagomé antiferromagnet,” [Phys. Rev. Lett. **68**, 855–858 \(1992\)](#).
- [101] K. Aoyama and H. Kawamura, “Spin ordering induced by lattice distortions in classical Heisenberg antiferromagnets on the breathing pyrochlore lattice,” [Phys. Rev. B **99**, 144406 \(2019\)](#).
- [102] A. Szabó and G. J. Nilsen, “Dynamics of the antiferromagnetic spin ice phase in pyrochlore spinels,” [arXiv:2305.16386 \[cond-mat\] \(2023\)](#).

- [103] D. L. Bergman, R. Shindou, G. A. Fiete, and L. Balents, “Models of degeneracy breaking in pyrochlore antiferromagnets,” [Phys. Rev. B **74**, 134409 \(2006\)](#).
- [104] T. Mizoguchi and M. Udagawa, “Flat-band engineering in tight-binding models: Beyond the nearest-neighbor hopping,” [Phys. Rev. B **99**, 235118 \(2019\)](#).
- [105] M. V. Gvozdikova and M. E. Zhitomirsky, “A monte carlo study of the first-order transition in a heisenberg fcc antiferromagnet,” [Journal of Experimental and Theoretical Physics Letters **81**, 236–240 \(2005\)](#).
- [106] R. Stübel and W. Janke, “Finite-size scaling of Monte Carlo simulations for the fcc Ising antiferromagnet: Effects of the low-temperature phase degeneracy,” [Phys. Rev. B **98**, 174413 \(2018\)](#).
- [107] P. Balla, Y. Iqbal, and K. Penc, “Degenerate manifolds, helimagnets, and multi- Q chiral phases in the classical Heisenberg antiferromagnet on the face-centered-cubic lattice,” [Phys. Rev. Research **2**, 043278 \(2020\)](#).

APPENDICES

Appendix A

Nearest Neighbours and Adjacency Matrices

A.1 Defining Adjacency Matrices

The Hamiltonian for spin systems segregated by k^{th} -neighbour interactions is

$$\mathcal{H} = \frac{1}{2} \sum_{jj'} \sum_k \mathcal{A}_{jj'}^{(k)} J_k \mathbf{S}_j \cdot \mathbf{S}_{j'}, \quad (\text{A.1})$$

where j, j' are site indices, J_k is the exchange coupling between k^{th} -nearest neighbours, and $\mathcal{A}_{jj'}^{(k)}$ is an adjacency coefficient such that

$$\mathcal{A}_{jj'}^{(k)} = \begin{cases} 1, & \text{if sites } j' \text{ and } j \text{ are } k^{\text{th}}\text{-nearest neighbours} \\ 0, & \text{otherwise} \end{cases}. \quad (\text{A.2})$$

Recall that the lattice used to model $\text{CuAlCr}_4\text{S}_8$, the breathing pyrochlore lattice, has the following primitive translation vectors from the face-centered-cubic (FCC) lattice:

$$\begin{aligned} \mathbf{a}_1 &= \frac{a}{2}(\hat{x} + \hat{y}), \\ \mathbf{a}_2 &= \frac{a}{2}(\hat{x} + \hat{z}), \\ \mathbf{a}_3 &= \frac{a}{2}(\hat{y} + \hat{z}), \end{aligned} \quad (\text{A.3})$$

where a is the edge-length of the cubic supercell. The breathing pyrochlore is non-Bravais, with a basis consisting of four sublattice sites:

$$\begin{aligned}\mathbf{r}_0 &= \mathbf{0}, \\ \mathbf{r}_1 &= \frac{\gamma}{\gamma+1}\mathbf{a}_1, \\ \mathbf{r}_2 &= \frac{\gamma}{\gamma+1}\mathbf{a}_2, \\ \mathbf{r}_3 &= \frac{\gamma}{\gamma+1}\mathbf{a}_3,\end{aligned}\tag{A.4}$$

where γ is the breathing ratio, which is ~ 1.07 for $\text{CuAlCr}_4\text{S}_8$ [33], meaning that the large tetrahedra are about 7% longer than the small tetrahedra in the lattice. To evaluate the Hamiltonian in Eq. (A.1), we need a definition for k^{th} -nearest neighbours for each k . For the purposes of this thesis, $k = \{1a, 1b, 2, 3a, 3b, 4, 5\}$. There are two types of first-nearest neighbours; $1a$ for neighbours that are on the same small tetrahedron, $1b$ for neighbours on the same large tetrahedron (shown in red and blue in Fig. A.1, respectively). There are also two types of third-nearest neighbours, which correspond to the same euclidean distance, but different graph-geodesic distances (the graph-geodesic distance between two sites on a breathing pyrochlore lattice is the minimum number of nearest-neighbour edges that are necessary to traverse when going between the two sites).

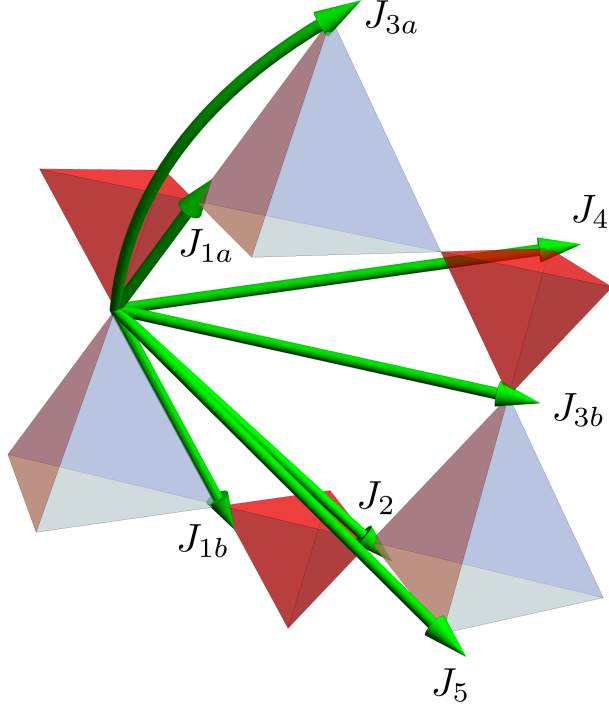


Figure A.1: Illustration of types of neighbours on a subset of the breathing pyrochlore, with sites on the corners of the tetrahedra.

For each type of neighbours k , let $\mathcal{N}_{cd}^{(k)}$ be the set of displacements between sublattice site c and all k^{th} -nearest neighbours that have a sublattice index d . From the sets that are written, the rest of the relevant sets can be determined by using

$$\mathcal{N}_{dc}^{(k)} = \left\{ -\mathbf{v} \mid \mathbf{v} \in \mathcal{N}_{cd}^{(k)} \right\}, \quad (\text{A.5})$$

where $\mathbf{v} \in \mathcal{N}_{cd}^{(k)}$ means that $\mathbf{v}$ is the displacement between some site with sublattice index c and a second site with sublattice index d that is a k^{th} -nearest neighbour to the first site.

With that in mind, the small-tetrahedra first-nearest neighbour displacement vectors are

$$\begin{aligned}
\mathcal{N}_{cc}^{(1a)} &= \emptyset \quad \text{for } c = 0, 1, 2, 3, \\
\mathcal{N}_{0,1}^{(1a)} &= \{-\mathbf{a}_1 + \mathbf{r}_1\}, \\
\mathcal{N}_{0,2}^{(1a)} &= \{-\mathbf{a}_2 + \mathbf{r}_2\}, \\
\mathcal{N}_{0,3}^{(1a)} &= \{-\mathbf{a}_3 + \mathbf{r}_3\}, \\
\mathcal{N}_{1,2}^{(1a)} &= \{\mathbf{a}_1 - \mathbf{a}_2 - (\mathbf{r}_1 - \mathbf{r}_2)\}, \\
\mathcal{N}_{1,3}^{(1a)} &= \{\mathbf{a}_1 - \mathbf{a}_3 - (\mathbf{r}_1 - \mathbf{r}_3)\}, \\
\mathcal{N}_{2,3}^{(1a)} &= \{\mathbf{a}_2 - \mathbf{a}_3 - (\mathbf{r}_2 - \mathbf{r}_3)\}.
\end{aligned} \tag{A.6}$$

The large-tetrahedra first-nearest neighbour displacements are

$$\begin{aligned}
\mathcal{N}_{cc}^{(1b)} &= \emptyset \quad \text{for } c = 0, 1, 2, 3, \\
\mathcal{N}_{0,1}^{(1b)} &= \{\mathbf{r}_1\}, \\
\mathcal{N}_{0,2}^{(1b)} &= \{\mathbf{r}_2\}, \\
\mathcal{N}_{0,3}^{(1b)} &= \{\mathbf{r}_3\}, \\
\mathcal{N}_{1,2}^{(1b)} &= \{\mathbf{r}_2 - \mathbf{r}_1\}, \\
\mathcal{N}_{1,3}^{(1b)} &= \{\mathbf{r}_3 - \mathbf{r}_1\}, \\
\mathcal{N}_{2,3}^{(1b)} &= \{\mathbf{r}_3 - \mathbf{r}_2\}.
\end{aligned} \tag{A.7}$$

Define the short hand: $\{\mathbf{u}_1, \mathbf{u}_2, \dots\} + \mathbf{w} := \{\mathbf{u}_1 + \mathbf{w}, \mathbf{u}_2 + \mathbf{w}, \dots\}$, then the 2nd-nearest-neighbour displacements are

$$\begin{aligned}
\mathcal{N}_{cc}^{(2)} &= \emptyset \quad \text{for } c \in \{0, 1, 2, 3\}, \\
\mathcal{N}_{01}^{(2)} &= \{\mathbf{a}_3 - \mathbf{a}_1, \mathbf{a}_2 - \mathbf{a}_1, -\mathbf{a}_2, -\mathbf{a}_3\} + \mathbf{r}_1, \\
\mathcal{N}_{02}^{(2)} &= \{\mathbf{a}_3 - \mathbf{a}_2, \mathbf{a}_1 - \mathbf{a}_2, -\mathbf{a}_1, -\mathbf{a}_3\} + \mathbf{r}_2, \\
\mathcal{N}_{03}^{(2)} &= \{\mathbf{a}_2 - \mathbf{a}_3, \mathbf{a}_1 - \mathbf{a}_3, -\mathbf{a}_1, -\mathbf{a}_2\} + \mathbf{r}_3, \\
\mathcal{N}_{12}^{(2)} &= \{\mathbf{a}_3 - \mathbf{a}_2, \mathbf{a}_1 - \mathbf{a}_3, \mathbf{a}_1, -\mathbf{a}_2\} + (\mathbf{r}_2 - \mathbf{r}_1), \\
\mathcal{N}_{13}^{(2)} &= \{\mathbf{a}_2 - \mathbf{a}_3, \mathbf{a}_1 - \mathbf{a}_2, \mathbf{a}_1, -\mathbf{a}_3\} + (\mathbf{r}_3 - \mathbf{r}_1), \\
\mathcal{N}_{23}^{(2)} &= \{\mathbf{a}_2 - \mathbf{a}_1, \mathbf{a}_1 - \mathbf{a}_3, -\mathbf{a}_3, \mathbf{a}_2\} + (\mathbf{r}_3 - \mathbf{r}_2).
\end{aligned} \tag{A.8}$$

The displacements corresponding to the 3rd-nearest neighbours are

$$\begin{aligned}
\mathcal{N}_{00}^{(3a)} &= \{\pm \mathbf{a}_1, \pm \mathbf{a}_2, \pm \mathbf{a}_3\}, \\
\mathcal{N}_{11}^{(3a)} &= \{\pm \mathbf{a}_1, \pm (\mathbf{a}_1 - \mathbf{a}_2), \pm (\mathbf{a}_1 - \mathbf{a}_3)\}, \\
\mathcal{N}_{22}^{(3a)} &= \{\pm \mathbf{a}_2, \pm (\mathbf{a}_2 - \mathbf{a}_1), \pm (\mathbf{a}_2 - \mathbf{a}_3)\}, \\
\mathcal{N}_{33}^{(3a)} &= \{\pm \mathbf{a}_3, \pm (\mathbf{a}_3 - \mathbf{a}_1), \pm (\mathbf{a}_3 - \mathbf{a}_2)\},
\end{aligned} \tag{A.9}$$

and

$$\begin{aligned}
\mathcal{N}_{00}^{(3b)} &= \{\pm (\mathbf{a}_1 - \mathbf{a}_2), \pm (\mathbf{a}_1 - \mathbf{a}_3), \pm (\mathbf{a}_2 - \mathbf{a}_3)\}, \\
\mathcal{N}_{11}^{(3b)} &= \{\pm \mathbf{a}_2, \pm (\mathbf{a}_2 - \mathbf{a}_3), \pm \mathbf{a}_3\}, \\
\mathcal{N}_{22}^{(3b)} &= \{\pm \mathbf{a}_1, \pm (\mathbf{a}_1 - \mathbf{a}_3), \pm \mathbf{a}_3\}, \\
\mathcal{N}_{33}^{(3b)} &= \{\pm \mathbf{a}_1, \pm \mathbf{a}_2, \pm (\mathbf{a}_1 - \mathbf{a}_2)\}.
\end{aligned} \tag{A.10}$$

The displacements for the 4th-nearest neighbours are

$$\mathcal{N}_{01}^{(4)} = \{-\mathbf{a}_1 - \mathbf{a}_2 + \mathbf{a}_3, -\mathbf{a}_1 + \mathbf{a}_2 - \mathbf{a}_3\} + \mathbf{r}_1 \tag{A.11}$$

$$\mathcal{N}_{02}^{(4)} = \{-\mathbf{a}_1 - \mathbf{a}_2 + \mathbf{a}_3, \mathbf{a}_1 - \mathbf{a}_2 - \mathbf{a}_3\} + \mathbf{r}_2,$$

$$\mathcal{N}_{03}^{(4)} = \{-\mathbf{a}_1 + \mathbf{a}_2 - \mathbf{a}_3, \mathbf{a}_1 - \mathbf{a}_2 - \mathbf{a}_3\} + \mathbf{r}_3,$$

$$\mathcal{N}_{12}^{(4)} = \{\mathbf{a}_1 - \mathbf{a}_2 - \mathbf{a}_3, \mathbf{a}_1 - \mathbf{a}_2 + \mathbf{a}_3\} + (\mathbf{r}_2 - \mathbf{r}_1),$$

$$\mathcal{N}_{13}^{(4)} = \{\mathbf{a}_1 - \mathbf{a}_2 - \mathbf{a}_3, \mathbf{a}_1 + \mathbf{a}_2 - \mathbf{a}_3\} + (\mathbf{r}_3 - \mathbf{r}_1),$$

$$\mathcal{N}_{23}^{(4)} = \{-\mathbf{a}_1 + \mathbf{a}_2 - \mathbf{a}_3, \mathbf{a}_1 + \mathbf{a}_2 - \mathbf{a}_3\} + (\mathbf{r}_3 - \mathbf{r}_2). \tag{A.12}$$

The displacements for the 5th-nearest neighbours are

$$\mathcal{N}_{01}^{(5)} = \{-\mathbf{a}_2 + \mathbf{a}_3, \mathbf{a}_2 - \mathbf{a}_3\} + \mathbf{r}_1,$$

$$\mathcal{N}_{02}^{(5)} = \{-\mathbf{a}_1 + \mathbf{a}_3, \mathbf{a}_1 - \mathbf{a}_3\} + \mathbf{r}_2,$$

$$\mathcal{N}_{03}^{(5)} = \{-\mathbf{a}_1 + \mathbf{a}_2, \mathbf{a}_1 - \mathbf{a}_2\} + \mathbf{r}_3,$$

$$\mathcal{N}_{12}^{(5)} = \{-\mathbf{a}_3, \mathbf{a}_3\} + (\mathbf{r}_2 - \mathbf{r}_1),$$

$$\mathcal{N}_{13}^{(5)} = \{-\mathbf{a}_2, \mathbf{a}_2\} + (\mathbf{r}_3 - \mathbf{r}_1),$$

$$\mathcal{N}_{23}^{(5)} = \{-\mathbf{a}_1, \mathbf{a}_1\} + (\mathbf{r}_3 - \mathbf{r}_2). \tag{A.13}$$

With these definitions,

$$\mathcal{A}_{cd}^{(k)}(\mathbf{q}) = \sum_{\mathbf{v} \in \mathcal{N}_{cd}^{(k)}} e^{i\mathbf{v} \cdot \mathbf{q}}, \tag{A.14}$$

and the Hamiltonian can be written as,

$$\mathcal{H} = \frac{1}{2} \sum_{\mathbf{q}, cd} \sum_k J_k \mathcal{A}_{cd}^{(k)}(\mathbf{q}) \sum_{\nu} s_c^{\nu}(\mathbf{q}) s_d^{\nu}(-\mathbf{q}), \quad (\text{A.15})$$

where

$$s_c^{\nu}(\mathbf{q}) = \sum_I s_{I,c}^{\nu} e^{i\mathbf{q} \cdot \mathbf{R}_{I,c}} \quad (\text{A.16})$$

for $\mathbf{R}_{I,c}$ being the position of site with cell index I and sublattice index c . $s_{I,c}^{\nu}$ is the ν -component of the spin at cell index I and sublattice index c . Thus,

$$\mathcal{H} = \frac{1}{2} \sum_{\mathbf{q}} \sum_{c,d=1}^4 \mathcal{J}_{cd}(\mathbf{q}) \sum_{\nu} s_c^{\nu}(\mathbf{q}) s_d^{\nu}(-\mathbf{q}) \quad (\text{A.17})$$

where the 4×4 exchange matrix in momentum space is

$$\mathcal{J}(\mathbf{q}) = \sum_k J_k \mathcal{A}^{(k)}(\mathbf{q}). \quad (\text{A.18})$$

A.2 Degeneracy Lines in the up-to-3rd-NN Model

$\mathcal{J}(\mathbf{q})$ is a 4×4 matrix since there are 4 sublattice sites which means that the Fourier transform block-diagonalizes the adjacency matrix into 4×4 blocks, as opposed to complete diagonalization that takes place in Bravais lattices. From Eq. (A.18), it is useful to analyze $\mathcal{J}(\mathbf{q})$ by observing shared properties of its constituent $\mathcal{A}^{(k)}$ matrices, which can be written as

$$\mathcal{A}_{cd}^{(k)}(\mathbf{q}) \propto \sum_n e^{i(\mathbf{r}_d - \mathbf{r}_c + \mathbf{R}_n) \cdot \mathbf{q}}, \quad (\text{A.19})$$

where $\mathbf{R}_n$ are some lattice translation vectors that depend on the neighbour type k and the matrix component c, d . We can see from this that

$$\mathcal{A}_{cd}^{(k)}(\mathbf{q}) \propto e^{i(\mathbf{r}_d - \mathbf{r}_c) \cdot \mathbf{q}}. \quad (\text{A.20})$$

This means that we can take a unitary transformation

$$\mathcal{A}^{(k)} \rightarrow W^{\dagger}(\mathbf{q}) \mathcal{A}^{(k)}(\mathbf{q}) W(\mathbf{q}), \quad (\text{A.21})$$

where

$$W = \text{diag} \left(1, e^{i(\mathbf{r}_1 - \mathbf{a}_1/2) \cdot \mathbf{q}}, e^{i(\mathbf{r}_2 - \mathbf{a}_2/2) \cdot \mathbf{q}}, e^{i(\mathbf{r}_3 - \mathbf{a}_3/2) \cdot \mathbf{q}} \right). \quad (\text{A.22})$$

Eq. (A.21) transforms the adjacency matrices into the forms of a regular (non-breathing) pyrochlore, by replacing $\mathbf{r}_1 \rightarrow \mathbf{a}_1/2$, $\mathbf{r}_2 \rightarrow \mathbf{a}_2/2$, $\mathbf{r}_3 \rightarrow \mathbf{a}_3/2$ as the effective sublattice vectors. This is so because the transformation in Eq. (A.21) replaces all the sublattice vectors of the breathing pyrochlores with the sublattice vectors of the regular pyrochlores. For that reason, we assume that the adjacency matrices $\mathcal{A}^{(k)}$ have underwent the transformation in Eq. (A.21) by the unitary matrix W defined in Eq. (A.22), which allows us to treat the lattice site positions as the regular pyrochlore's lattice site positions. Since the adjacency matrices are only affected by unitary transformations when adjusting the geometric breathing ratio of the lattice, this means that asymmetry between the sizes of the up-tetrahedra and down-tetrahedra does not affect the eigenvalues of the exchange coupling matrix. For this reason, we assume that the lattice positions are the same ones as that of the regular non-breathing pyrochlore, since this assumption does not change the eigenvalues (energy bands) of the exchange coupling.

Consider the matrix, which is the nearest-neighbour matrix for zero wavevector,

$$\begin{aligned} A_0 &= \begin{pmatrix} 0 & 1 & 1 & 1 \\ 1 & 0 & 1 & 1 \\ 1 & 1 & 0 & 1 \\ 1 & 1 & 1 & 0 \end{pmatrix} \\ &= \begin{pmatrix} 1 & 1 & 1 & 1 \\ 1 & -1 & -1 & 1 \\ -1 & 1 & -1 & 1 \\ -1 & -1 & 1 & 1 \end{pmatrix} \begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 3 \end{pmatrix} \begin{pmatrix} 1 & 1 & 1 & 1 \\ 1 & -1 & -1 & 1 \\ -1 & 1 & -1 & 1 \\ -1 & -1 & 1 & 1 \end{pmatrix}^{-1}, \quad (\text{A.23}) \end{aligned}$$

then the first-nearest-neighbour matrices can be expressed as

$$\begin{aligned} \mathcal{A}^{(1a)} &= \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & e^{i\frac{\mathbf{a}_1}{2} \cdot \mathbf{q}} & 0 & 0 \\ 0 & 0 & e^{i\frac{\mathbf{a}_2}{2} \cdot \mathbf{q}} & 0 \\ 0 & 0 & 0 & e^{i\frac{\mathbf{a}_3}{2} \cdot \mathbf{q}} \end{pmatrix} A_0 \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & e^{-i\frac{\mathbf{a}_1}{2} \cdot \mathbf{q}} & 0 & 0 \\ 0 & 0 & e^{-i\frac{\mathbf{a}_2}{2} \cdot \mathbf{q}} & 0 \\ 0 & 0 & 0 & e^{-i\frac{\mathbf{a}_3}{2} \cdot \mathbf{q}} \end{pmatrix}, \\ \mathcal{A}^{(1b)} &= \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & e^{-i\frac{\mathbf{a}_1}{2} \cdot \mathbf{q}} & 0 & 0 \\ 0 & 0 & e^{-i\frac{\mathbf{a}_2}{2} \cdot \mathbf{q}} & 0 \\ 0 & 0 & 0 & e^{-i\frac{\mathbf{a}_3}{2} \cdot \mathbf{q}} \end{pmatrix} A_0 \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & e^{i\frac{\mathbf{a}_1}{2} \cdot \mathbf{q}} & 0 & 0 \\ 0 & 0 & e^{i\frac{\mathbf{a}_2}{2} \cdot \mathbf{q}} & 0 \\ 0 & 0 & 0 & e^{i\frac{\mathbf{a}_3}{2} \cdot \mathbf{q}} \end{pmatrix}. \quad (\text{A.24}) \end{aligned}$$

Note that if $A = PA_0P^{-1}$ and $A_0\mathbf{v} = \lambda\mathbf{v}$ for some eigenvector $\mathbf{v}$ of A_0 , then $A(P\mathbf{v}) = PA_0P^{-1}(P\mathbf{v}) = \lambda(P\mathbf{v})$. Using that property, $\mathcal{A}^{(1a)}$ has eigenvectors and eigenvalues of the form

$$\left\{ \begin{pmatrix} 1 \\ e^{i\frac{\mathbf{a}_1}{2}\cdot\mathbf{q}} \\ -e^{i\frac{\mathbf{a}_2}{2}\cdot\mathbf{q}} \\ -e^{i\frac{\mathbf{a}_3}{2}\cdot\mathbf{q}} \end{pmatrix}, \begin{pmatrix} 1 \\ -e^{i\frac{\mathbf{a}_1}{2}\cdot\mathbf{q}} \\ e^{i\frac{\mathbf{a}_2}{2}\cdot\mathbf{q}} \\ -e^{i\frac{\mathbf{a}_3}{2}\cdot\mathbf{q}} \end{pmatrix}, \begin{pmatrix} 1 \\ -e^{i\frac{\mathbf{a}_1}{2}\cdot\mathbf{q}} \\ -e^{i\frac{\mathbf{a}_2}{2}\cdot\mathbf{q}} \\ e^{i\frac{\mathbf{a}_3}{2}\cdot\mathbf{q}} \end{pmatrix} \right\} \text{ with eigenvalue } -1,$$

$$\begin{pmatrix} 1 \\ e^{i\frac{\mathbf{a}_1}{2}\cdot\mathbf{q}} \\ e^{i\frac{\mathbf{a}_2}{2}\cdot\mathbf{q}} \\ e^{i\frac{\mathbf{a}_3}{2}\cdot\mathbf{q}} \end{pmatrix} \text{ with eigenvalue } 3. \quad (\text{A.25})$$

$\mathcal{A}^{(1b)}$ has eigenvectors and eigenvalues of the form

$$\left\{ \begin{pmatrix} 1 \\ e^{-i\frac{\mathbf{a}_1}{2}\cdot\mathbf{q}} \\ -e^{-i\frac{\mathbf{a}_2}{2}\cdot\mathbf{q}} \\ -e^{-i\frac{\mathbf{a}_3}{2}\cdot\mathbf{q}} \end{pmatrix}, \begin{pmatrix} 1 \\ -e^{-i\frac{\mathbf{a}_1}{2}\cdot\mathbf{q}} \\ e^{-i\frac{\mathbf{a}_2}{2}\cdot\mathbf{q}} \\ -e^{-i\frac{\mathbf{a}_3}{2}\cdot\mathbf{q}} \end{pmatrix}, \begin{pmatrix} 1 \\ -e^{-i\frac{\mathbf{a}_1}{2}\cdot\mathbf{q}} \\ -e^{-i\frac{\mathbf{a}_2}{2}\cdot\mathbf{q}} \\ e^{-i\frac{\mathbf{a}_3}{2}\cdot\mathbf{q}} \end{pmatrix} \right\} \text{ with eigenvalue } -1,$$

$$\begin{pmatrix} 1 \\ e^{-i\frac{\mathbf{a}_1}{2}\cdot\mathbf{q}} \\ e^{-i\frac{\mathbf{a}_2}{2}\cdot\mathbf{q}} \\ e^{-i\frac{\mathbf{a}_3}{2}\cdot\mathbf{q}} \end{pmatrix} \text{ with eigenvalue } 3. \quad (\text{A.26})$$

Noting the relationship between the neighbours:

$$\begin{aligned} \mathcal{N}^{(2)} &= \{1a \text{ neighbors of } 1b \text{ neighbors and } 1b \text{ neighbors of } 1a, \\ &\quad \text{different sublattice indices from each other}\}, \\ \mathcal{N}^{(3a)} &= \{1a \text{ neighbors of } 1b \text{ neighbors and } 1b \text{ neighbors of } 1a, \\ &\quad \text{same sublattice indices}\}, \\ \mathcal{N}^{(3b)} &= \{1a \text{ neighbors of } 1b \text{ neighbors of } 1a \text{ neighbors,} \\ &\quad \text{same sublattice indices}\}. \end{aligned} \quad (\text{A.27})$$

By utilizing the definition of the adjacency matrices in Eq. (A.14), and using the statements in Eq. (A.27), then the adjacency matrices can be expressed in terms of matrix products, given as

$$\begin{aligned}
\mathcal{A}^{(2)} &= \mathcal{A}^{(1a)}\mathcal{A}^{(1b)} + \mathcal{A}^{(1b)}\mathcal{A}^{(1a)} - \mathcal{A}^{(3a)}, \\
\mathcal{A}^{(3a)} &= \text{diag}(\mathcal{A}^{(1a)}\mathcal{A}^{(1b)} + \mathcal{A}^{(1b)}\mathcal{A}^{(1a)}), \\
\mathcal{A}^{(3b)} &= \text{diag}(\mathcal{A}^{(1a)}\mathcal{A}^{(1b)}\mathcal{A}^{(1a)}).
\end{aligned} \tag{A.28}$$

Evaluating the matrices on the degeneracy line $\mathbf{q} = 2\pi/a(1, q, 0)$:

$$\mathcal{A}^{(3a)}(2\pi/a(1, q, 0)) = \mathcal{A}^{(3b)}(2\pi/a(1, q, 0)) = \begin{pmatrix} -2 & 0 & 0 & 0 \\ 0 & -2 & 0 & 0 \\ 0 & 0 & -2 & 0 \\ 0 & 0 & 0 & -2 \end{pmatrix} = -2\mathbb{I}, \tag{A.29}$$

Thus, for wavevectors along the degeneracy line, using the top equation in Eq. (A.28) along with Eq.(A.29), we find

$$\mathcal{A}^{(2)} = \mathcal{A}^{(1a)}\mathcal{A}^{(1b)} + \mathcal{A}^{(1b)}\mathcal{A}^{(1a)} + 2\mathbb{I}. \tag{A.30}$$

Let

$$\begin{aligned}
\mathbf{v}_\lambda^{\mathcal{A}} &:= \text{any eigenvector of } \mathcal{A} \text{ with eigenvalue } \lambda, \\
\mathcal{E}_\lambda^{\mathcal{A}} &:= \text{eigenspace of } \mathcal{A} \text{ with eigenvalue } \lambda.
\end{aligned} \tag{A.31}$$

Using the eigenvectors listed in Eqs. (A.25) and (A.26), what happens on the degeneracy line is that

$$\begin{aligned}
\mathbf{v}_3^{\mathcal{A}^{(1a)}} \cdot \mathbf{v}_3^{\mathcal{A}^{(1b)}} &= 1 + e^{i\mathbf{q} \cdot \mathbf{a}_1} + e^{i\mathbf{q} \cdot \mathbf{a}_2} + e^{i\mathbf{q} \cdot \mathbf{a}_3} = 1 - e^{2iq} - 1 + e^{2iq} = 0 \\
\Rightarrow \mathbf{v}_3^{\mathcal{A}^{(1a)}} &\text{ is orthogonal to } \mathbf{v}_3^{\mathcal{A}^{(1b)}} \text{ and thus is in the eigenspace } \mathcal{E}_{-1}^{\mathcal{A}^{(1b)}}, \\
\mathbf{v}_3^{\mathcal{A}^{(1b)}} &\text{ is orthogonal to } \mathbf{v}_3^{\mathcal{A}^{(1a)}} \text{ and thus is in the eigenspace } \mathcal{E}_{-1}^{\mathcal{A}^{(1a)}}.
\end{aligned} \tag{A.32}$$

This degeneracy of the adjacency matrices' eigenspaces exists due to the geometry of the pyrochlore's adjacency matrix [104]. The rest of the vector space is $\mathcal{E}_{-1}^{\mathcal{A}^{(1b)}} \cap \mathcal{E}_{-1}^{\mathcal{A}^{(1a)}}$ which is two-dimensional as an intersection of three-dimensional eigenspaces. Thus, letting

$$\mathcal{J} = J_{1a}\mathcal{A}^{(1a)} + J_{1b}\mathcal{A}^{(1b)} + J_2\mathcal{A}^{(2)} + J_{3a}\mathcal{A}^{(3a)} + J_{3b}\mathcal{A}^{(3b)}, \tag{A.33}$$

and substituting for $\mathbf{q} = 2\pi/a(1, q, 0)$ in the degeneracy line, using Eqs.(A.28), and (A.29):

$$\begin{aligned}\mathcal{J}(q) &= J_{1a}\mathcal{A}^{(1a)} + J_{1b}\mathcal{A}^{(1b)} + J_2(\mathcal{A}^{(1a)}\mathcal{A}^{(1b)} + \mathcal{A}^{(1b)}\mathcal{A}^{(1a)} + 2\mathbb{I}) \\ &\quad + J_{3a}(-2\mathbb{I}) + J_{3b}(-2\mathbb{I}).\end{aligned}\tag{A.34}$$

$$\begin{aligned}\Rightarrow \mathcal{J}(q) &= J_2(\mathcal{A}^{(1a)}\mathcal{A}^{(1b)} + \mathcal{A}^{(1b)}\mathcal{A}^{(1a)}) + J_{1a}\mathcal{A}^{(1a)} + J_{1b}\mathcal{A}^{(1b)} \\ &\quad + 2(J_2 - J_{3a} - J_{3b})\mathbb{I}.\end{aligned}\tag{A.35}$$

Taking the eigenvector $\mathbf{u}_1 = \begin{pmatrix} 1 \\ e^{-i\frac{\mathbf{a}_1}{2} \cdot \mathbf{q}} \\ e^{-i\frac{\mathbf{a}_2}{2} \cdot \mathbf{q}} \\ e^{-i\frac{\mathbf{a}_3}{2} \cdot \mathbf{q}} \end{pmatrix}$ where

$$\begin{aligned}\mathcal{A}^{(1a)}\mathbf{u}_1 &= 3\mathbf{u}_1, \\ \mathcal{A}^{(1b)}\mathbf{u}_1 &= -\mathbf{u}_1,\end{aligned}\tag{A.36}$$

then $\mathbf{u}_1$ is an eigenvector of $\mathcal{J}(q)$, since

$$\begin{aligned}\Rightarrow \mathcal{J}(q)\mathbf{u}_1 &= [J_2(3(-1) + (-1)3) + J_{1a}(3) + J_{1b}(-1) + 2(J_2 - J_{3a} - J_{3b})]\mathbf{u}_1 \\ &= [-4J_2 + 3J_{1a} - J_{1b} - 2(J_{3a} + J_{3b})]\mathbf{u}_1.\end{aligned}\tag{A.37}$$

Taking the eigenvector $\mathbf{u}_2 = \begin{pmatrix} 1 \\ e^{i\frac{\mathbf{a}_1}{2} \cdot \mathbf{q}} \\ e^{i\frac{\mathbf{a}_2}{2} \cdot \mathbf{q}} \\ e^{i\frac{\mathbf{a}_3}{2} \cdot \mathbf{q}} \end{pmatrix}$ where

$$\begin{aligned}\mathcal{A}^{(1a)}\mathbf{u}_2 &= -\mathbf{u}_2, \\ \mathcal{A}^{(1b)}\mathbf{u}_2 &= 3\mathbf{u}_2,\end{aligned}\tag{A.38}$$

then $\mathbf{u}_2$ is an eigenvector of $\mathcal{J}(q)$, since

$$\begin{aligned}\mathcal{J}(q)\mathbf{u}_2 &= [J_2((-1)3 + 3(-1)) + J_{1a}(-1) + J_{1b}(3) + 2(J_2 - J_{3a} - J_{3b})]\mathbf{u}_2 \\ &= [-4J_2 - J_{1a} + 3J_{1b} - 2(J_{3a} + J_{3b})]\mathbf{u}_2.\end{aligned}\tag{A.39}$$

Taking eigenvector $\mathbf{u}_3$ from the two-dimensional degenerate eigenspace, $\mathcal{E}_{-1}^{\mathcal{A}^{(1b)}} \cap \mathcal{E}_{-1}^{\mathcal{A}^{(1a)}}$, then

$$\begin{aligned}\Rightarrow \mathcal{J}(q)\mathbf{u}_3 &= [J_2((-1)(-1) + (-1)(-1)) + J_{1a}(-1) + J_{1b}(-1) + 2(J_2 - J_{3a} - J_{3b})]\mathbf{u}_3 \\ &= [4J_2 - (J_{1a} + J_{1b}) - 2(J_{3a} + J_{3b})]\mathbf{u}_3,\end{aligned}\tag{A.40}$$

where $\mathbf{u}_3$ is an eigenvector from the two-dimensional eigenspace $\mathcal{E}_{-1}^{\mathcal{A}^{(1b)}} \cap \mathcal{E}_{-1}^{\mathcal{A}^{(1a)}}$. We thus find that the eigenvalue of $\mathcal{J}(q)$ for eigenvector $\mathbf{u}_3$, which is $[4J_2 - (J_{1a} + J_{1b}) - 2(J_{3a} + J_{3b})]$, is two-fold degenerate. All the eigenvalues for wavevectors on the degeneracy lines are thus exhausted in Eqs.(A.37) , (A.39), (A.40), giving the eigenvalues

$$\begin{aligned}\epsilon_1 &= -4J_2 - J_{1a} + 3J_{1b} - 2(J_{3a} + J_{3b}), \\ \epsilon_2 &= -4J_2 + 3J_{1a} - J_{1b} - 2(J_{3a} + J_{3b}), \\ \epsilon_3 &= \epsilon_4 = 4J_2 - (J_{1a} + J_{1b}) - 2(J_{3a} + J_{3b}),\end{aligned}\tag{A.41}$$

which do not depend on $\mathbf{q}$ when on the degeneracy line $\mathbf{q} = 2\pi/a(1, q, 0)$. If the exchange couplings $\{J_{1a}, J_{1b}, J_2, J_{3a}, J_{3b}\}$ are such that one of $\epsilon_1, \epsilon_2, \epsilon_3, \epsilon_4$ is the absolute minimum of the energy bands, then we get a case like the up-to-3rd-NN model for CuAlCr₄S₈, where the ordering wavevectors are along the degeneracy lines.

A.2.1 4th and 5th Nearest Neighbours

Let

$$D = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & e^{i\mathbf{r}_1 \cdot \mathbf{q}} & 0 & 0 \\ 0 & 0 & e^{i\mathbf{r}_2 \cdot \mathbf{q}} & 0 \\ 0 & 0 & 0 & e^{i\mathbf{r}_3 \cdot \mathbf{q}} \end{pmatrix}.\tag{A.42}$$

Define

$$\mathcal{A}^{(4)}(\mathbf{q}) = D^\dagger \tilde{\mathcal{A}}^{(4)} D,\tag{A.43}$$

where

$$\begin{aligned}\tilde{\mathcal{A}}^{(4)}(\mathbf{q}) = & 2 \begin{pmatrix} 0 & e^{-i\mathbf{a}_1 \cdot \mathbf{q}} \cos[(\mathbf{a}_2 + \mathbf{a}_3) \cdot \mathbf{q}] & e^{-i\mathbf{a}_2 \cdot \mathbf{q}} \cos[(\mathbf{a}_1 + \mathbf{a}_3) \cdot \mathbf{q}] & e^{-i\mathbf{a}_3 \cdot \mathbf{q}} \cos[(\mathbf{a}_1 + \mathbf{a}_2) \cdot \mathbf{q}] \\ e^{i\mathbf{a}_1 \cdot \mathbf{q}} \cos(\mathbf{a}_2 + \mathbf{a}_3) \cdot \mathbf{q} & 0 & e^{i(\mathbf{a}_1 - \mathbf{a}_2) \cdot \mathbf{q}} \cos(\mathbf{a}_3 \cdot \mathbf{q}) & e^{i(\mathbf{a}_1 - \mathbf{a}_3) \cdot \mathbf{q}} \cos(\mathbf{a}_2 \cdot \mathbf{q}) \\ e^{i\mathbf{a}_2 \cdot \mathbf{q}} \cos(\mathbf{a}_1 + \mathbf{a}_3) \cdot \mathbf{q} & e^{-i(\mathbf{a}_1 - \mathbf{a}_2) \cdot \mathbf{q}} \cos(\mathbf{a}_3 \cdot \mathbf{q}) & 0 & e^{i\mathbf{a}_2 \cdot \mathbf{q}} \cos[(\mathbf{a}_1 - \mathbf{a}_3) \cdot \mathbf{q}] \\ e^{i\mathbf{a}_3 \cdot \mathbf{q}} \cos[(\mathbf{a}_1 + \mathbf{a}_2) \cdot \mathbf{q}] & e^{-i(\mathbf{a}_1 - \mathbf{a}_3) \cdot \mathbf{q}} \cos(\mathbf{a}_2 \cdot \mathbf{q}) & e^{-i\mathbf{a}_2 \cdot \mathbf{q}} \cos[(\mathbf{a}_1 - \mathbf{a}_3) \cdot \mathbf{q}] & 0 \end{pmatrix}.\end{aligned}\tag{A.44}$$

Let

$$\mathcal{A}^{(5)}(\mathbf{q}) = D^\dagger \tilde{\mathcal{A}}^{(5)} D,\tag{A.45}$$

where

$$\tilde{\mathcal{A}}^{(5)}(\mathbf{q}) = 2 \begin{pmatrix} 0 & \cos[(\mathbf{a}_2 - \mathbf{a}_3) \cdot \mathbf{q}] & \cos[(\mathbf{a}_1 - \mathbf{a}_3) \cdot \mathbf{q}] & \cos[(\mathbf{a}_1 - \mathbf{a}_2) \cdot \mathbf{q}] \\ \cos[(\mathbf{a}_2 - \mathbf{a}_3) \cdot \mathbf{q}] & 0 & \cos(\mathbf{a}_3 \cdot \mathbf{q}) & \cos(\mathbf{a}_2 \cdot \mathbf{q}) \\ \cos[(\mathbf{a}_1 - \mathbf{a}_3) \cdot \mathbf{q}] & \cos(\mathbf{a}_3 \cdot \mathbf{q}) & 0 & \cos(\mathbf{a}_1 \cdot \mathbf{q}) \\ \cos[(\mathbf{a}_1 - \mathbf{a}_2) \cdot \mathbf{q}] & \cos(\mathbf{a}_2 \cdot \mathbf{q}) & \cos(\mathbf{a}_1 \cdot \mathbf{q}) & 0 \end{pmatrix}. \quad (\text{A.46})$$

Including the contribution of 4th-NN and 5th-NN adjacency matrices breaks the degeneracy line that is seen in the up-to-3rd-NN model. This can be seen by adding $J_4 \mathcal{A}^{(4)}(\mathbf{q}) + J_5 \mathcal{A}^{(5)}(\mathbf{q})$ terms to the right side of Eq. (A.18), and calculating the eigenvalues, which are no longer degenerate along the degeneracy lines of the up-to-3rd-NN model [$\mathbf{q} = 2\pi/a(1, q, 0)$].

Appendix B

FCC Results

B.1 Classical Monte Carlo

Face-centered-cubic (FCC) lattice models can not fully describe the breathing pyrochlore [63], but interactions between tetrahedra can be viewed as effective FCC nearest-neighbour interactions. Since the FCC lattice is the underlying Bravais lattice for the breathing pyrochlore, we expect the results to be different but analogous. The antiferromagnetic nearest-neighbour FCC is a frustrated system that undergoes first-order phase transition below a critical temperature [105, 106]. Nearest-neighbour AFM Heisenberg model on the FCC lattice has degeneracy line at $\mathbf{q}_s = 2\pi/a(1, q, 0)$, similar to the up-to-3rd-NN model on the pyrochlore lattice, although thermal order by disorder selects special wavevectors of the form $\mathbf{Q}_1 := 2\pi/a(1, 0, 0)$ and $\mathbf{Q}_3 := 2\pi/a(1, 1/2, 0)$, which correspond respectively to the so-called AFM1 and AFM3 configurations [3, 105]. past classical Monte Carlo simulations have shown that thermal order by disorder leads to selection of the AFM1 state in the nearest-neighbour AFM Heisenberg model on the FCC lattice [3]. However, by adding further-neighbour interactions, it is possible to get ordering wavevectors of the form $(q, q, 0)$, (q, q, q) or $(q, 0, 0)$, where q depends on the exchange couplings [107]. The nearest-neighbour AFM FCC model was reproduced individually from Monte Carlo simulations, and structure factors are shown in Figs. B.1 and B.2. By observing the peaks at the lowest temperatures in Fig. B.1, we see that the structure factor peaks at $\mathbf{Q} = 2\pi/a(1, 0, 0)$, which is the AFM1 configuration defined in Ref. [3]. The observation of peaks at the AFM1 wavevector in individual's classical Monte Carlo agrees with literature [3].

FCC lattice, nearest-neighbour AFM , $[hk0]$ plane, Monte Carlo structure factor

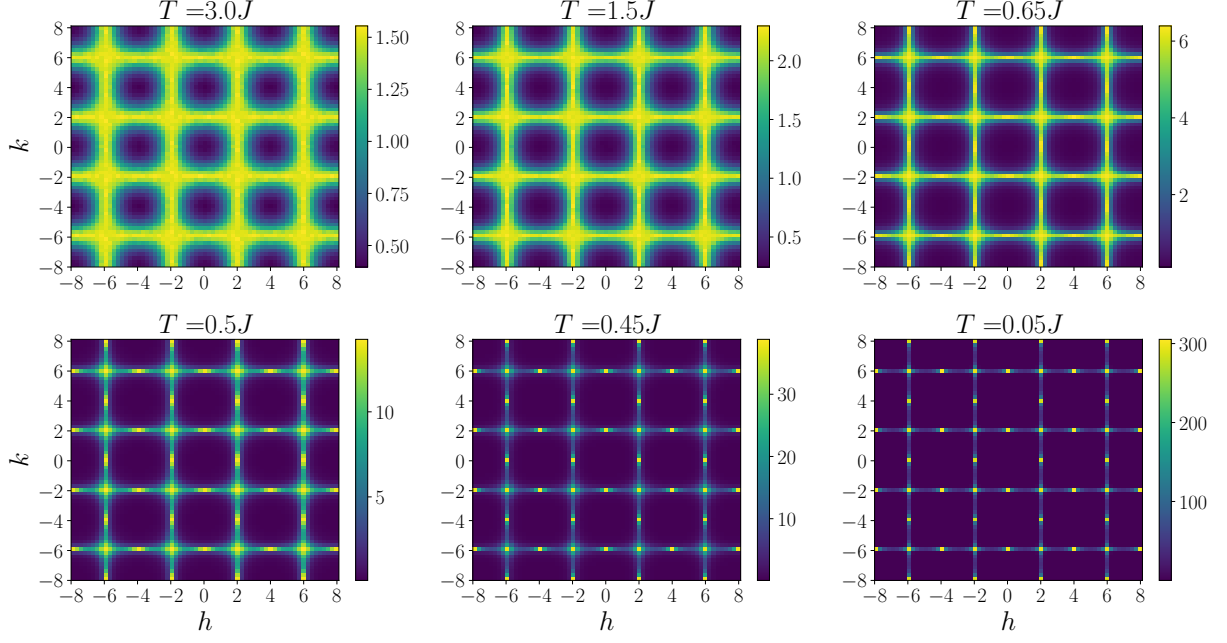


Figure B.1: Structure factor for FCC lattice from Monte Carlo simulations along the $[hk0]$ plane for $16 \times 16 \times 16$ unit cells. The wavevector represented by $[hk0]$ is $\mathbf{Q} = \frac{\pi}{a}(h\hat{x} + k\hat{y})$.

FCC lattice, nearest-neighbour AFM , $[hhl]$ plane, Monte Carlo structure factor

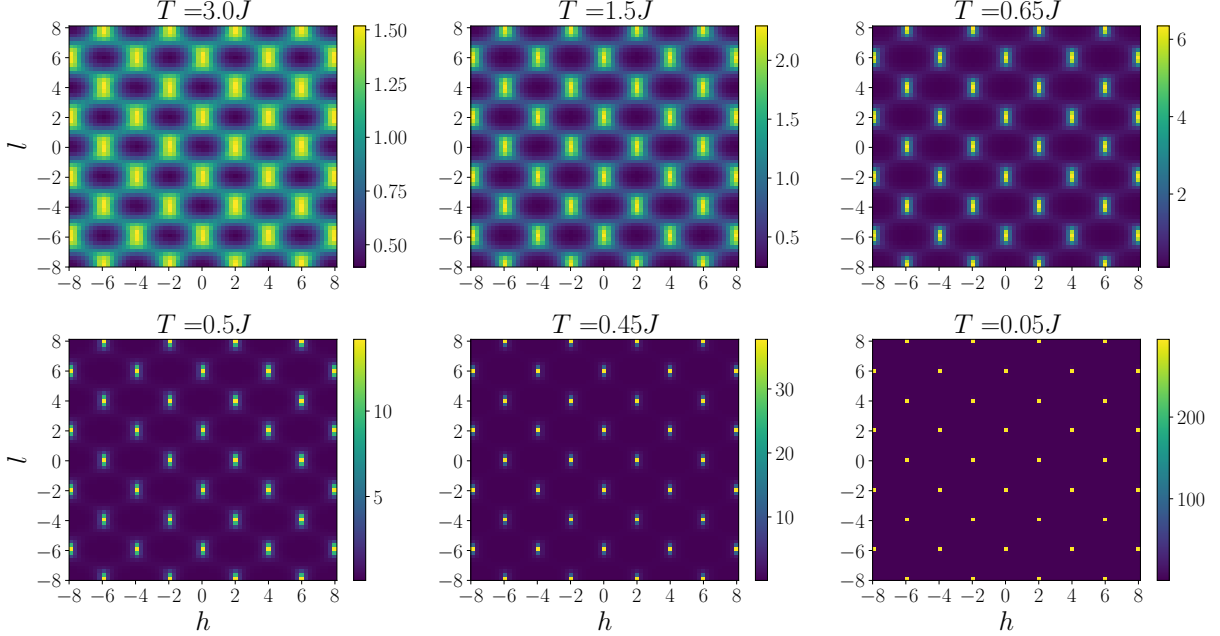


Figure B.2: Structure factor for nearest-neighbour AFM Heisenberg model on the FCC lattice from Monte Carlo simulations along the $[hhl]$ plane for $16 \times 16 \times 16$ unit cells. The wavevector represented by $[hhl]$ is $\mathbf{Q} = \frac{\pi}{a}(h\hat{x} + h\hat{y} + l\hat{z})$.

B.2 Large- N and Mean-Field Theory

While Monte Carlo simulations for the nearest-neighbour AFM model on the FCC lattice show selections within the degeneracy lines, in the case of large- N and MFT, the structure factor maintains a constant intensity along the degeneracy lines, as seen in Fig. B.3. This lack of modulation along the degeneracy lines is due to the absence of a wavevector-dependent form factor for the unit cell, as the FCC lattice is Bravais. In contrast, the up-to-3rd-NN model for $\text{CuAlCr}_4\text{S}_8$, which has the same ground-state degeneracy line as the FCC model, does have modulations along the degeneracy lines due to the form factor of the tetrahedral unit cell, as discussed in Section 3.3.2 While only the plot for the large- N structure factor is shown in Fig. B.3, the MFT structure factor has the same behaviour (constant intensity along the degeneracy line with intensity that grows as temperature decreases).

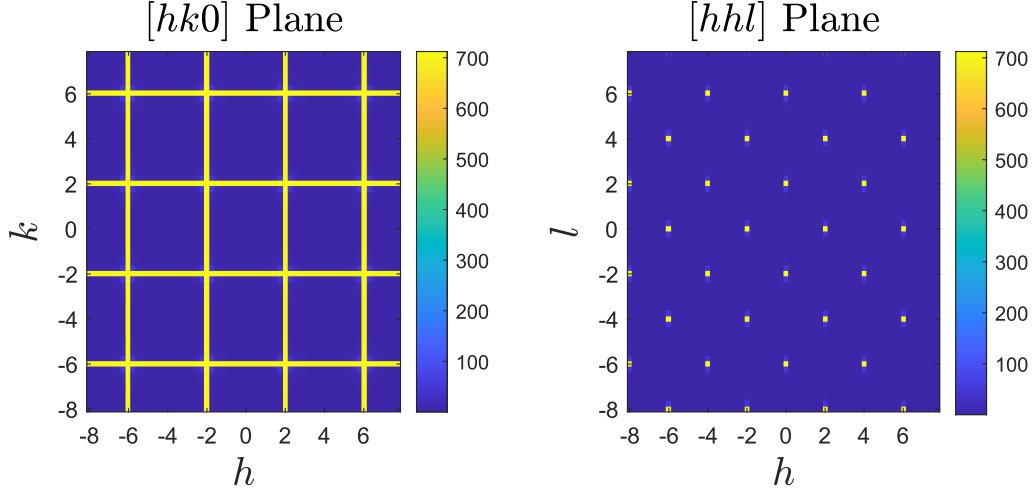


Figure B.3: Structure factor for nearest-neighbour AFM Heisenberg on the FCC lattice from large- N for $16 \times 16 \times 16$ unit cells. The wavevector represented by $[hk0]$ is $\mathbf{Q} = \frac{\pi}{a}(h\hat{x} + k\hat{y})$, and for $[hhl]$ the wavevector is $\mathbf{Q} = \frac{\pi}{a}(h\hat{x} + h\hat{y} + l\hat{z})$. Note that the wavevectors forms uniform-intensity peaks along the degeneracy lines in the $[hk0]$ plane, in contrast to the discrete peaks seen for the Monte Carlo structure factor in Fig. B.1.

B.3 Summary of Appendix B

The FCC lattice is a useful model for comparing with the breathing pyrochlore, since the breathing pyrochlore's underlying Bravais lattice is FCC. The nearest-neighbour AFM Heisenberg model on the FCC lattice and the up-to-3rd-NN model both have ground-state degeneracy lines of the form $\mathbf{q}_s = 2\pi/a(1, q, 0)$. Unlike the up-to-3rd-NN model on the breathing pyrochlore, the MFT and large- N structure factors along the degeneracy lines in the FCC model are constant, while the up-to-3rd-NN model have continuous variations along the degeneracy lines for the same methods. as discussed in Sections 3.2.2 and 3.3.2 for the up-to-3rd-NN model, the variation of the structure factor in MFT and large- N along the degeneracy lines is due to the unit cell's form factors, which is wavevector-dependent for the tetrahedral unit cells for the non-Bravais breathing pyrochlore lattice. On the other hand, the FCC lattice's unit form factor is constant. From classical Monte Carlo simulations, the structure factor for the FCC has peaks at wavevectors of the form $\mathbf{Q}_1 = 2\pi/a(1, 0, 0)$, in both the literature (Ref. [3]) and individual's replication. This is in contrast to individual's large- N and MFT results for the FCC model, where the structure

factor is constant along the degeneracy line (as shown in Fig. B.3). The selection of the $\mathbf{Q}_1 = 2\pi/a(1, 0, 0)$ ordering wavevector in classical Monte Carlo simulations of the FCC lattice is due to order by disorder [3]. While awaiting rigorous mathematical proof, order by disorder is a candidate explanation for the Bragg peaks in the structure factor that were observed from Monte Carlo simulations in the up-to-3rd-NN model, shown in Fig. 4.8.