Thermodynamics of anisotropic triangular magnets with ferro- and antiferromagnetic exchange

Burkhard Schmidt and Peter Thalmeier
Max-Planck-Institut für Chemische Physik fester Stoffe, D-01187 Dresden, Germany
E-mail: bs@cpfs.mpg.de

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Abstract
We investigate thermodynamic properties like specific heat \( c_V \) and susceptibility \( \chi \) in anisotropic \( J_1-J_2 \) triangular quantum spin systems \((S = 1/2)\). As a universal tool we apply the finite temperature Lanczos method (FTLM) based on exact diagonalization of finite clusters with periodic boundary conditions. We use clusters up to \( N = 28 \) sites where the thermodynamic limit behavior is already stably reproduced. As a reference we also present the full diagonalization of a small eight-site cluster. After introducing model and method we discuss our main results on \( c_V(T) \) and \( \chi(T) \). We show the variation of peak position and peak height of these quantities as function of control parameter \( J_2/J_1 \). We demonstrate that maximum peak positions and heights in Néel phase and spiral phases are strongly asymmetric, much more than in the square lattice \( J_1-J_2 \) model. Our results also suggest a tendency to a second side maximum or shoulder formation at lower temperature for certain ranges of the control parameter. We finally explicitly determine the exchange model of the prominent triangular magnets \( \text{Cs}_2\text{CuCl}_4 \) and \( \text{Cs}_2\text{CuBr}_4 \) from our FTLM results.

1. Introduction

The 2D triangular \( S = 1/2 \) Heisenberg antiferromagnet (HAF) is the archetypical geometrically frustrated quantum magnet [1]. Therefore it has been studied in countless investigations. Although there is no pure physical realization due to in-plane symmetry breaking and inter-plane coupling several compounds fall into the wider class of anisotropic triangular magnets where the exchange coupling \( J_2 \) along one of the triangle sides is different from \( J_1 \) along the other two sides [2]. In fact this generalization is not a drawback but opens interesting possibilities. It allows to consider a smooth interpolation between square lattice HAF to isotropic triangular magnet to quasi-1D chain compounds as function of a single tuning parameter \( J_2/J_1 \).

Most of the work on this magnetic system was focused on the zero temperature phase diagram as function of anisotropy ratio, spin wave excitations and influence of quantum fluctuations as well as effects of external fields like plateau formation in the magnetization. We will not touch these fundamental topics but refer to [2] and references cited therein. Here we will focus on a more practical issue, namely the determination of the exchange constant or at least their anisotropy ratio from thermodynamic quantities of triangular magnets. This can be done by analyzing the experimental temperature dependence of specific heat and magnetic susceptibility where the former is less favorable due to lattice contributions [3]. A simplified but not unambiguous determination of exchange constants is possible by identifying position and height of the maximum in thermodynamic quantities and comparing with theoretical predictions. Further useful tools of diagnosing the exchange model are magnetothermals, e.g. magnetocaloric properties as well as high field magnetization and saturation field. This program has sofar mainly been carried out for frustrated \( J_1-J_2 \) square lattice magnets [4–6].

Here we focus on the numerical investigation of much less studied finite temperature properties of anisotropic triangular quantum spin systems. Previous investigations used variants of Monte Carlo methods for the quantum case [7–9], also for the classical case [10, 11] or analytical methods for the low temperature regime [12] and high temperature series expansion [13]. In the present work we use the finite temperature Lanczos method (FTLM) based on the exact diagonalization (ED) of finite lattice tiles for this purpose. The method is
based on evaluating the partition function by averaging over random starting vectors in the ED procedure. Using periodic boundary conditions and discrete symmetries we can go up to largest cluster size of $N = 28$ sites for thermodynamic averages. We also consider smaller clusters of size $N = 16$, 20, 24 by FTLM. Furthermore we present the full analytical solution of the spectrum for the smallest $N = 8$ cluster as a reference point. However, we note that unlike zero temperature ED results for finite clusters the FTL method cannot be used for finite size scaling analysis of thermodynamic quantities. Nonetheless in the special case of the 1D chain system ($J_2 = 0$) we can compare to exact results which are in excellent agreement with the $N = 28$ cluster results. This indicates that our FTLM results are trustworthy to use as a representation for the thermodynamic limit.

Our main emphasis is the calculation of peak position $T_{\text{max}}$ and height $C_{\text{V}}(T_{\text{max}})$ and $\chi(T_{\text{max}})$ in the temperature dependence of specific heat and susceptibility, respectively. We investigate its systematic variation with anisotropy control parameter $J_2/J_1$ or $\phi = \tan^{-1}(J_2/J_1)$, in particular when it is tuned between the simple special cases mentioned above. This information is of great importance for the analysis of thermodynamic data of triangular magnets. The $T_{\text{max}}$ ($\phi$) dependence turns out to be considerably more asymmetric than for the related square lattice model [4]. We show that in certain ranges of the control parameter an indication of second maximum or shoulder in these quantities appears. Furthermore as an example we discuss the analysis of the full temperature dependence of $\chi(T)$ for the most prominent triangular quantum spin systems $\text{Cs}_2\text{CuCl}_4$ and the isostructural $\text{Cs}_2\text{CuBr}_4$ using FTLM results. We demonstrate that the derived exchange model is in excellent agreement with the one obtained from direct spectroscopic methods like inelastic neutron scattering (INS, $\text{Cs}_2\text{CuCl}_4$ only) spin wave results and electron spin resonance (ESR) experiments, both in high fields.

In section 2 we define the model and its parametrization. The reference of the full solution for the eight-site cluster is discussed in section 3. The FTL method and its technical implementation are discussed to some extent in section 4. Our main results on specific heat and susceptibility are presented in sections 5 and 6, respectively and the explicit comparison to $\text{Cs}_2\text{CuCl}_4$ and $\text{Cs}_2\text{CuBr}_4$ is discussed in section 7. Finally section 8 gives the conclusion and outlook.

2. Anisotropic triangular exchange model and its parametrization

The anisotropic $J_1-J_2$ exchange model on the triangular lattice (figure 1) is given by

$$\mathcal{H} = \sum_{\langle ij \rangle} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j$$

(1)

with

$$J_{ij} = \begin{cases} J_1 & \text{if } \mathbf{R}_{ij} = \mathbf{R}_i \pm \frac{1}{2} (\mathbf{e}_x \pm \sqrt{3} \mathbf{e}_y), \\ J_2 & \text{if } \mathbf{R}_i = \mathbf{R}_j \pm \mathbf{e}_x, \end{cases}$$

(2)

where $\mathbf{e}_x$, $\mathbf{e}_y$ are unit vectors along cartesian directions. Figure 1 may also be interpreted as tilted square lattice model with one diagonal $J_2$ bond cut out [2]. For the anisotropic triangular-lattice model, different parametrizations of the exchange energies are customary. As introduced in [4] and used subsequently we prefer the polar representation defined by

$$J_1 = J_c \cos \phi, \quad J_2 = J_c \sin \phi,$$

(3)
\[ J_c = \sqrt{J_1^2 + J_2^2}, \quad \phi = \tan^{-1}\left(\frac{J_2}{J_1}\right), \]

where \( J_c \) gives the overall energy scale and \( \phi \) is the anisotropy control parameter. This parametrization allows for an easy interpolation between important geometrical limiting cases, namely the square-lattice Néel antiferromagnet with \( J_2 = 0 \ (\phi = 0) \), the isotropic 120° triangular antiferromagnet with \( J_2 = J_1 \ (\phi = \pi/4) \), the antiferromagnetic chain with \( J_1 = 0 \ (\phi = \pi/2) \), and their ferromagnetic counterparts. However, there are alternative possibilities in the literature which we briefly mention here for ease of comparison (figure 2). Many authors regard the model as an extension to the one-dimensional spin chain, therefore they use the exchange \( J_2 \) along these chains as the overall energy unit and parametrize their results in terms of \( \alpha := J_2/J_1 \) with \( J_1 \) being the interchain coupling. From a square-lattice perspective in turn, the exchange parameter \( J_1 \) appears to be the natural energy unit, and correspondingly \( 1/\alpha := J_2/J_1 \) is used as well.

Both model parameters \( \alpha \) and \( 1/\alpha \) are problematic when trying to describe the full phase diagram, in particular the interpolation between the square-lattice antiferromagnet (\( \alpha \to \infty \)) and the one-dimensional chain (\( 1/\alpha \to \infty \)). To overcome this, the function \( f := J_2/(J_1 + J_2) = 1/(1 + \alpha) \) has been introduced in \([14]\), which remains finite in both limits and between these.

However the latter parametrization also does not cover the full phase diagram unambiguously, which is why we have introduced the universal energy scale \( J_c \) and the anisotropy angle \( \phi \). In the square-lattice case, this has the additional advantage that \( J_c \), apart from a global factor \( \sqrt{2} \), denotes the magnetocaloric energy scale \( J_m \) as well \([4]\). To facilitate the comparison of our results with the literature, figure 2 displays the dependence of the quantities introduced here on the anisotropy control parameter \( \phi \).

The nearest neighbor (n.n.) HAF model on the triangular lattice is the generic ‘geometrically frustrated’ spin system where the exchange energy of n.n. bonds cannot be minimized simultaneously for all bonds (see upper corner of figure 1). It is worthwhile to quantify this intuitive notion of ‘frustration’. A measure for it is the total loss of exchange energy due to frustration relative to the exchange energy without it. For the basic triangular (three-site) plaquette in figure 1 the degree of frustration is then given by

\[ \kappa (\phi) := 1 - \frac{E_\triangle}{E_i + E_d}. \]  

(4)

Here \( E_\triangle \) is the ground state energy of the frustrated triangle. \( E_i := E_\triangle (J_2 = 0) \) and \( E_d := E_\triangle (J_1 = 0) \) are the ground state energies of its unfrustrated trimer and dimer parts, respectively with

\[ E_\triangle (\phi) := \min \left\{ -\frac{3}{4} J_2, -\frac{1}{2} J_1 + \frac{1}{4} J_2, \frac{1}{4} J_1 + \frac{1}{4} J_2 \right\}, \]

(5)

where the minimum is taken from the three different energy eigenvalues of the triangle. Using these expressions in equation (4) the degree of frustration (in per cent) in the triangular HAF as function of control parameter is shown in figure 3. There the dotted lines indicate the classical boundaries between FM, AF and spiral phases as discussed in \([2]\). \( \kappa (\phi) \) vanishes identically in the unfrustrated (\( J_2 < 0 \) or \( \phi < 0 \)) case. In the frustrated regime (\( J_2 > 0 \) or \( \phi > 0 \)) it achieves its maximum values of \( \kappa = 4/7 \) corresponding to 57% frustration at the isotropic point (\( \Delta \)) and the spiral/FM phase boundary while it vanishes for the 1D chain case (\(|\rangle \)) where \( J_1 = 0 \). We note that the reduction in the ordered ground state moment in the frustrated regime does not directly follow the degree of frustration but is the result of the subtle interplay of the latter with quantum fluctuations \([2]\).
3. Precursor: classical phase diagram and eight-site full solution

Within the FTLM the thermodynamic quantities will be computed directly using an averaging procedure over the low energy spectrum only. To obtain a better intuition for the triangular Heisenberg model it is useful to calculate also the full spectrum by direct diagonalization of small clusters. We will demonstrate that it develops characteristic signatures at the classical phase boundaries and special symmetry points as function of control parameter using the eight-site cluster.

3.1. Spectrum and classical phase diagram

As discussed in [4] for the square-lattice model, we can express the spectrum of the triangular eight-site cluster on tile 8:2-2 with periodic boundary conditions as a sum over Hamiltonians on complete graphs. We define

\[ H^{CG}_{\mathcal{L}} = \sum_{i \in \mathcal{L}} S_i \cdot S_j = \frac{1}{2} \left( \sum_{i \in \mathcal{L}} S_i \right)^2 - \sum_{i \in \mathcal{L}} S_i^2 \],

where \( \mathcal{L} \) denotes an ordered list of lattice sites. In our case it has either two elements (a bond), four elements (a square or tetrahedron), or eight elements (a cube). We then can write

\[ H_8 = J_1 \left( H^{CG}_{[1,2,3,4,5,6,7,8]} - \left( H^{CG}_{[1,3,4,5]} + H^{CG}_{[2,6,7,8]} \right) \right) + 2J_2 \left( H^{CG}_{[1,3]} + H^{CG}_{[2,4]} + H^{CG}_{[3,4]} + H^{CG}_{[5,6,7,8]} \right) \]

for the Hamiltonian. The tile and its labelling is illustrated in figure 4. From equation (7) with \( S = 1/2 \) being the maximum expectation value for each local spin \( S_i \), we get the corresponding list of eigenvalues by hierarchically constructing all possible multiple-spin configurations starting with the basic two-spin singlets and triplets on the pairs \{1, 5\}, \{3, 4\}, \{2, 8\}, and \{6, 7\}: from all pairs of two-spin states, we can construct the four-spin states with total spin \( S = 0, 1, 2, 3, 4 \) and spin degeneracy \( S(S+1) \). Because the total spin may be composed in several ways by the spins of sub-clusters there exist additional degeneracies. In this way, we can construct a total of \( \binom{N}{N/2} = 70 \) states for the eight-site cluster.

Table 1 displays the complete set of eigenvalues, together with their (additional) degeneracies, total spins, and total spins on the sub-lattices. Of particular interest are those states corresponding to classical ground states (marked by an asterisk in the last column): the columnar antiferromagnet (first state in the table, energy \(-6J_2\)), the Néel antiferromagnet (seventh state, energy \(2J_2 - 6J_0\)), and the ferromagnet (last state, energy \(2(2J_0 + J_2)\)). These three states replace each other as ground states as a function of the anisotropy ratio \( \phi \), see figure 5. Figure 5 displays the full spectrum of the tile 8:2-2 as a function of the anisotropy angle. The thicknesses of the lines indicate the degeneracies of the corresponding states as listed in table 1. Solid lines denote singlet states, the long-dashed line denotes the ferromagnet, for further line types see the figure caption.

We overlay this spectrum to the classical phase diagram of the model discussed in detail in [2]. The classical FM, AF and spiral phases are separated by the thin vertical lines. The thin dotted lines indicate as special cases the...
square-lattice Néel antiferromagnet (□, $\phi = 0$ or $J_1 > 0$, $J_2 = 0$), isotropic antiferromagnetic triangular lattice ($\bigtriangleup$, $\phi = \pi/4$ or $J_2 \equiv J_1 > 0$) corresponding to the non-collinear 120° commensurate spiral structure and one-dimensional antiferromagnetic chains ($\|$, $\phi = \pi/2$ or $J_1 = 0$, $J_2 > 0$).

Characteristic for the spectrum at these six special points is the high number of degenerate excited states with different total spin. At the borders of the classical ferromagnetic phase also the ground state changes from the
fully polarized state to a singlet. However the classical phase boundary between the antiferromagnet and the spiral phase does not correspond to an equivalent change of (in this case nonmagnetic) ground states. This is due to the fact that with our eight-site tile we cannot approximate any incommensurate state at all, therefore the ‘best’ approximation to the ‘true’ ground state remains the Néel state for $J_1 \leq J_2$ (equivalent to $0.148 \leq \phi/\pi \leq 0.205$), and the columnar antiferromagnetic state for larger values of $J_2/J_1$.

Similar to the square-lattice case [4], we observe level crossings near the classical phase boundary between AF and spiral phase. For the square lattice, we took this as an indication for the appearance of a nonmagnetic phase, coinciding with the suppression of the ordered moment in a region around the classical transition observed within linear spin-wave theory [2]. Qualitatively the same happens here, however this analogy should not be taken too far, because no indication of that kind exists for the classically invisible crossover to one-dimensional chains at $\phi = \pi/2$, which is in reality surrounded by a large nonmagnetic region. And empirically we know that linear spin-wave theory rather underestimates the size of these nonmagnetic regions. At the crossover from the spiral to the ferromagnetic phase for $0.852 \phi/\pi \approx 1$, a similar type of pattern of level crossings exists. Linear spin-wave theory gives inconsistent results in this case.

3.2. Thermodynamics of the eight-site cluster

Given the eigenvalue $E_i$ with degeneracy $d_i$ and total spin $S_i$ for each state $i$ listed in table 1, we can easily evaluate the partition function $Z = \sum_i d_i \left(2S_i + 1\right) e^{-\beta E_i}$ to calculate the magnetic susceptibility $\chi$ and the specific heat $c_V$ according to

$$\chi = \frac{\beta L}{N Z} \sum_i d_i \left(2S_i + 1\right) \frac{S_i}{3} e^{-\beta E_i},$$

$$c_V = \frac{\beta L}{N Z} \left[ \frac{1}{Z} \sum_i d_i \left(2S_i + 1\right) E_i^2 e^{-\beta E_i} \right] - \left[ \frac{1}{Z} \sum_i d_i \left(2S_i + 1\right) E_i e^{-\beta E_i} \right]^2,$$

where $\beta = 1/(k_B T)$ with $k_B$ being the Boltzmann constant. Here and in the following, we express the molar susceptibility in units of $N_L \mu_0 (g \mu_B)^2 J_c^{-1}$, where $N_L$ is the Loschmidt constant, $\mu_0$ the magnetic permeability constant, $g$ the gyromagnetic ratio, and $\mu_B$ the Bohr magneton. For the dimension of the specific heat $c_V$, we use the universal gas constant $R = N_L k_B$. 

Figure 5. Energy spectrum of the eight-site cluster, classified according to total spin $S$. Solid lines: $S = 0$, short-dashed lines: $S = 1$, dotted lines: $S = 2$, dash-dotted lines: $S = 3$, long-dashed lines: $S = 4$. The line thickness indicates the degeneracy of the corresponding energy level, see table 1. The thin vertical lines denote the classical phase boundaries between ferromagnet (FM), Néel antiferromagnet (AF), and spiral structure. The dotted vertical lines denote the three special cases square-lattice Néel antiferromagnet ($J_2 \equiv J_1 > 0$), isotropic triangular lattice ($J_1 \equiv J_2 > 0$), and one-dimensional antiferromagnetic chains ($J_1 = 0, J_2 > 0$).
4. General remarks on finite temperature methods

The finite temperature properties of spin systems can be treated with analytical high temperature expansions [13, 15–18] or with the numerical FTL method [19] which will be employed in this work. As a reference we first discuss briefly the single first order term of the expansion method.

4.1. High temperature approximation

The high-temperature behavior of the susceptibility $\chi$ and the specific heat $c_V$ to quadratic order in $\beta$ is determined by the Curie–Weiss energy $\Theta$ and the magnetocaloric energy scale $J_{mc}$, which are defined through

$$\Theta = \frac{S(S+1)}{3} \sum_n J_{i+n} = \frac{J_1 + J_2}{2},$$

$$J_{mc}^2 = \frac{1}{2} \sum_n J_{i+n}^2 = 2J_1^2 + J_2^2.$$ (11)

The sums run over all bonds $n$ connecting an arbitrary but fixed site $i$ with its (not necessarily nearest) neighbors at sites $|i + n|$. We then have [18]

$$\chi = \frac{S(S+1)}{3} \beta L (1 - \beta \Theta),$$

$$c_V = \frac{1}{3} [S(S+1)]^{2} \beta \Theta J_{mc}^2.$$ (13)

In principle we should be able to determine the exchange parameters $J_1$ and $J_2$ already from high-temperature fits of the experimental results to the expressions above. However having fixed $J_{mc}$ and $\Theta$ determines $2J_1 + J_2$ and $|J_1 - 4J_2|$ but leaves the sign of the latter undetermined. When expressed with the parameters $L$ and $\phi_i$ this is equivalent to the fact that there are, apart from special cases, always two possible values $\phi_i$ for the anisotropy parameter. These two values $\phi_i$, however, can lie in two different thermodynamic phases with completely different properties. This ambiguity is similar to the one in the square lattice case [24], adapted to the triangular lattice. There are two important differences: at finite temperatures we cannot easily perform any kind of finite-size scaling analysis of the partition function, therefore we directly take the results of the different lattice tilings. In addition there exists at least one phase corresponding to a classical phase with an incommensurate ordering vector. Due to the finiteness of our $k$ space grid, we cannot model this closely. However for thermodynamic properties like susceptibility and heat capacity all thermally populated states contribute, and the exact modeling of the ground state as a function of our parameters is of secondary importance. For zero temperature ED approach the introduction of twisted boundary conditions may provide a way to circumvent this problem [25].

We attempt to determine the thermal expectation value of an arbitrary static operator $A$ by the fundamental traces over the statistical operator,
\[ (A)_{\beta} = \frac{1}{\mathcal{Z}} \sum_{n=1}^{N_e} \left\{ n \left| e^{-\beta H} A \right| n \right\}, \]  
\[ \mathcal{Z} = \sum_{n=1}^{N_e} \left\{ n \left| e^{-\beta H} \right| n \right\}, \]  

where \( \mathcal{Z} \) is the partition function and \( N_e \) is the dimension of the Hilbert space spanned by the basis \( \{ \left| n \right\rangle : n = 1 \ldots N_e \} \) (\( N_e \approx 2.7 \cdot 10^8 \) for \( N = 28 \)). In each symmetry-invariant subspace of the full Hilbert space, the Lanczos algorithm in principle is a sophisticated iterative basis change transforming the original Hamiltonian \( H \) to an equivalent one for an open one-dimensional chain (not ring) problem with complex on-site potentials and n.n. interactions. Each iteration step corresponds to adding an additional site to this chain. After \( M \) steps, the resulting equivalent tridiagonal Hamiltonian matrix \( M H \) can be diagonalized easily to get the eigenvalues \( \{ \psi_j : j = 1 \ldots M \} \) such that we can, in principle, evaluate equation (14). The moduli of the additional matrix elements of \( M H \) rapidly decrease with increasing number of iterations \( M \), a property which we use as a convergence criterion. Furthermore the difference in ground-state energy for iteration \( M \) and \( M - 1 \) is used as a second convergence criterion. Typical values such that machine precision is reached for the ground state energy are \( M = \mathcal{O}(100) \), which is vanishingly small compared to the original dimension \( N_e \approx \mathcal{O}(10^8) \) of the Hilbert space. To sample an as large as possible part of the Hilbert space, we start \( N_R = \mathcal{O}(100) \) iterations with different random wave functions or starting vectors \( \left| r \right\rangle \), such that eventually we use no more than \( \mathcal{O}(10^4) \) eigenvalues and wave functions per Hamiltonian block. It may be shown [19] that this procedure yields an asymptotically exact result. In summary, the thermal expectation value of \( A \) is approximated by

\[ \langle A \rangle_{\beta} \approx \frac{1}{\mathcal{Z}} \sum_{s} \sum_{i=1}^{N_s} \sum_{r=1}^{M_s} e^{-\beta \epsilon_i} \langle r_i \psi_j \rangle \langle \psi_j | A | r_i \rangle, \]  

where the index \( s \) denotes the summation over all symmetry sectors of the Hilbert space with dimension \( N_s \). If the operator \( A \) is a conserved quantity with \( [H, A] = 0 \), we can replace \( A \) by its quantum numbers \( A_j \), and equation (16) further simplifies to

\[ \langle A \rangle_{\beta} \approx \frac{1}{\mathcal{Z}} \sum_{s} \sum_{i=1}^{N_s} \sum_{r=1}^{M_s} e^{-\beta \epsilon_i} A_j \langle r_i \psi_j \rangle \langle \psi_j | A_j | r_i \rangle. \]  

The general definitions of the volume magnetic susceptibility and the heat capacity are

\[ \chi_V = \mu_0 \lim_{B_0 \to 0} \frac{\partial^2 F}{\partial B_0^2}, \quad C_V = -\frac{k_B}{\beta} \left( \frac{\partial^2}{\partial \beta^2} \right) F, \]  

where \( H = B_0 / \mu_0 \) is the external magnetic field defining the z direction and \( F = (-1/\beta) \ln \mathcal{Z} \) is the canonical free energy. Written in terms of the expectation values defined above, we get the cumulants.
\[
\chi = \frac{\beta B}{N} \left( \left\langle \Omega_z^2 \right\rangle - \left\langle \Omega_z \right\rangle^2 \right), \quad (20)
\]

\[
c_V = \frac{\beta^2}{N} \left( \left\langle H_z^2 \right\rangle - \left\langle H_z \right\rangle^2 \right) \quad (21)
\]

for the molar susceptibility and the specific heat of a tile with \(N\) sites, respectively. In our case, both \(\Omega_z\) and \(H\) trivially commute with \(\mathbf{H}\), allowing us to use equation (18) to determine the thermal expectation values. Furthermore spontaneous magnetic order is absent because our tiles are finite and we do not include an external magnetic field, therefore we can safely set \(\left\langle \Omega_z \right\rangle = 0\).

As mentioned before, in the comparison of calculated values and experimental results two strategies are possible. One can identify the maximum position and value of thermodynamic quantities or perform a fit over the whole temperature range to extract the exchange model parameters. We will discuss both approaches.

5. Heat capacity

First we discuss the heat capacity which requires only the cluster eigenvalues for its evaluation. A comparison of the theoretical temperature dependence to experiments is, however, not straightforward due to the lattice contribution to the heat capacity [3].

5.1. Temperature dependence

To demonstrate characteristic features, figures 7 and 8 show the temperature dependence of the specific heat \(c_V(T)\) according to equation (21) for a selected range of anisotropy parameters \(\phi\) in the antiferromagnetic phase (figure 7) and the spiral phase (figure 8). The FTLM calculations are trustworthy only down to a temperature range of \(T \approx \Delta J/N k_B\). For lower temperatures they are dominated by the artificial finite size gaps. This excluded region is indicated by grey bars in the figures.

For the AF phase with values \(-0.4 \leq \phi/\pi \leq -0.21\) a single peak indicated by dots that shifts continuously to higher values with increasing \(\phi\) is observed. This is qualitatively clear already from the eight-site spectrum (figure 5) which shows an increasing average excitation gap from the ground state in that range of \(\phi\).

Furthermore a plateau (or very flat second maximum) at the lowest temperatures close to the finite size gap region is visible.

For the spiral phase the values \(0.25 \leq \phi/\pi \leq 0.44\), correspond to the region between the isotropic triangular lattice with \(J_2/J_1 = 1\) and deep inside the disordered phase with quasi-one-dimensional chains (\(J_2/J_1 \approx 5\)). The tile 28:2-4 was used for the numerical calculations in both cases.

In figure 8, the characteristic maxima of \(c_V(T)\), indicated by the small black dots in the figure, have positions which fall into two different temperature ranges: For the isotropic triangular case with \(\phi/\pi = 0.25\), the maximum sits at \(T_{\Delta} \approx 0.18 J_1/k_B\), reducing in magnitude and shifting slightly to lower temperatures \(T_{\Delta} \approx 0.15 J_1/k_B\) upon increasing \(\phi\) from its isotropic value to \(\phi/\pi \approx 0.31\) or \(J_2/J_1 \approx 1.5\). At this point, a second maximum develops starting at \(T_{\Delta} \approx 0.32 J_1/k_B\), shifting to higher temperatures as \(\phi\) is increased towards the disordered region. Furthermore, the maximum \(T_{\Delta}\) characteristic for the triangular lattice rapidly disappears with increasing \(\phi\). Only the \(C_V(T)\) curves for \(\phi/\pi = 0.31\) and \(\phi/\pi = 0.32\) show both maxima simultaneously. At

\[\text{Figure 7. Temperature dependence of the specific heat } c_V(T) \text{ of the anisotropic triangular lattice according to equation (21) for anisotropy parameters } \phi \text{ in the antiferromagnetic phase ranging between } \phi/\pi = -0.4 \text{ and } \phi/\pi = -0.21, \text{ see legend. We used tile 28:2-4 for the numerical evaluation of equation (21), the grey-shaded area at low temperatures illustrates the finite-size gap of order } \mathcal{O}(J/N). \text{ The characteristic maxima of } c_V(T) \text{ are indicated by the small black dots.}\]
high temperatures $T \gg J_0/k_B$, all curves show the $(1/T)^2$ temperature dependence expected from equation (13).

5.2. Exchange anisotropy dependence of peak position and value

Figure 9 shows a compilation of the maximum positions and values of $C_f(T)$ for the five different tiles we have used as a function of the anisotropy parameter $\phi$. The solid lines denote the exact solution for the tile 8:2-2, see equation (9) and table 1. The black dots denote the maxima for the tile 16:4-0, the open triangles for the tile 20:2-4, the solid diamonds for the tile 24:4-0, the open squares for the tile 28:2-4. Furthermore, the exact results taken from [26] for the one-dimensional chain, $C_f(T_{\text{max}})/(N_0 k_B) = 0.35$ and $k_B T_{\text{max}}/J_0 = 0.481$, are marked with the white circles and serve as a gauge to judge how close a cluster of given size approaches the thermodynamic limit.

The eight-site cluster, introduced as an illustration of the model and its overall spectrum, clearly is not very useful quantitatively to discuss the heat capacity in the thermodynamic limit. Only the overall behavior of the maximum temperature is qualitatively similar to our findings for the larger tilings, however the two minima in the spiral phase are shifted towards the classical phase borders. The values $C_f(T_{\text{max}})$ for the eight-site cluster are monotonically increasing in the antiferromagnetic phase, followed by a minimum at $\phi/\pi \approx 0.1$ and a maximum at the isotropic point, $\phi/\pi = 0.25$. On the ferromagnetic-$J_1$ side for $1/2 < \phi/\pi < 1$, $C_f(T_{\text{max}})$ increases again to a second maximum, followed by a minimum at the crossover to the ferromagnet at $J_2/J_1 = 1/2$. At the one-dimensional point $J_1 = 0$, naturally both $T_{\text{max}}$ and $C_f(T_{\text{max}})$ differ strongly from the exact values.

Also the 16-site tiling shows similar features. For the larger clusters of size $N = 20$ and more, both maximum temperature positions and maximum values of the specific heat clearly show a double-peak structure as function of $\phi$. The positions $T_{\text{max}}$ decrease with increasing cluster size, apart from the regions around the isotropic point and in the spiral phase near the ferromagnet. At the one-dimensional point, agreement with the infinite-chain result [26] (white circles) is achieved already with $N = 20$ tiling. And therefore results for the $N = 28$ tile represent well the thermodynamic limit as far as peak position and height is concerned. Denoting the largest value in each sector of figure 9 by $T_{\text{max}}^\alpha$, we observe that $T_{\text{max}}^\alpha (AF)/T_{\text{max}}^\alpha (\text{spiral}) = 1.58$. This asymmetry in $T_{\text{max}}^\alpha (\phi)$ is considerably larger than the corresponding one in the square lattice $J_1/J_2$ model where $T_{\text{max}}^\alpha (AF)/T_{\text{max}}^\alpha (\text{CAF}) = 1.26$. (The columnar AF (CAF) phase replaces the spiral phase in this model.)

Similarly for the asymmetry ratios of peak values in the triangular case we get $C_f(T_{\text{max}}^\alpha) (AF)/C_f(T_{\text{max}}^\alpha) (\text{spiral}) = 1.51$ much larger than $C_f(T_{\text{max}}^\alpha) (AF)/C_f(T_{\text{max}}^\alpha) (\text{CAF}) = 1.10$ in the square lattice. Inside the AF and spiral sectors the lowest $T_{\text{max}}$ is reached close to the isotropic triangular point with $T_{\text{max}}^\alpha \approx 0.18J_0/k_B$ because there exchange frustration is most pronounced (figure 3). This leads to a high density of low energy excitations (see figure 5) and therefore a low $T_{\text{max}}^\Delta$.

Furthermore, in parts of the antiferromagnetic as well as the spiral phase, a second maximum $C_f(T_{\text{max}}^2)$ at very low temperatures appears. $T_{\text{max}}^2$ depends roughly linearly on $\phi$ while $C_f(T_{\text{max}}^2)$ remains constant and small, see also figure 7. With the 28-site tiling being the largest possible, we cannot judge whether this second-low temperature maximum in the antiferromagnetic phase merely is a finite-size effect. This is different from the situation in the spiral phase, where the partially observed second maximum is at temperatures $T_{\text{max}}^2$ far larger than the finite-size gap, see also figure 8.
Similar to the behavior around the isotropic point, at the crossover to the ferromagnetic region a second maximum gradually appears in $c_{V}(T)$ which then evolves to the ‘ferromagnetic’ maximum while the ‘spiral’ maximum disappears. This also happens at comparatively low temperatures with an irregular behavior of the maximum values as function of $\phi$. We attribute this irregularity to the fact that in particular near the borders of the spiral phase the ground state and possible low-lying excited states have incommensurate ordering vectors $Q_{ AF} + \delta Q$ and $Q_{ FM} + \delta Q$ respectively with $|\delta Q| \ll 1$. These are not contained in the coarse grid of crystal momenta of our finite tiles.

6. Susceptibility

Evaluation of the susceptibility with FTLM is more involved because it requires the calculation of magnetic moment matrix elements. On the other hand this quantity can be more easily compared to experimental results. Most known exchange parameters for spin systems are due to the application of this method.

6.1. Temperature dependence

Similar to the specific heat, we have calculated the temperature dependence of the static magnetic susceptibility $\chi(T)$ according to equation (20) with the tilings shown in figure 6. Figure 10 shows the results in a selected range of the anisotropy parameter, $0.57 \leq \phi/\pi \leq 0.86$, calculated with tiling 28:2-4. This parameter range corresponds to the interpolation between ferromagnetically coupled ($J_{1} < 0$) quasi-one-dimensional antiferromagnetic chains with $J_{2}/J_{1} \approx -4.5$ and the crossover to the ferromagnet at the classical boundary $J_{2}/J_{1} = -1/2$. For the former, a very broad maximum is characteristic which gradually evolves into the $T = 0$ divergence of $\chi(T)$ in the ferromagnetic phase, which is the expected behavior.
6.2. Exchange anisotropy dependence

In the same way as for the specific heat, we follow the positions and values of the characteristic maxima of \( \chi(T) \) as a function of the anisotropy parameter, using the tiles displayed in figure 6 again. This is shown in figure 11. The solid lines denote the eight-site results according to equation (8). For the same reasons as discussed for the heat capacity, strong deviations from the larger tilings occur in particular in the spiral phase. In contrast to \( c_V(T) \), the maximum positions and values of \( \chi(T) \) are already converged for tilings of size \( N = 20 \) and larger, apart from

![Figure 10. Temperature dependence of the static susceptibility \( \chi(T) \) of the anisotropic triangular lattice according to equation (20) for anisotropy parameters \( \phi \) in the spiral phase ranging between \( \phi/\pi = 0.57 \) and \( \phi/\pi = 0.86 \), see legend. We used tile 28:2-4 for the numerical evaluation of equation (20), the gray-shaded area at low temperatures illustrates the finite-size gap of order \( \mathcal{O}(J/N) \). The characteristic maxima of \( \chi(T) \) are indicated by the small black dots.](image)

![Figure 11. Maximum positions (top) and values (bottom) of the static susceptibility \( \chi(T) \) as a function of the anisotropy parameter \( \phi \). Solid lines: exact solution for tile 8:2-2, squares: tile 16:4-0, triangles: tile 20:2-4, diamonds: tile 24:4-0, filled circles: tile 28:2-4. The white rings mark the corresponding exact values for the one-dimensional chain [26].](image)
the crossover to the ferromagnetic phase, where a tile-dependence of the maximum temperatures clearly can be observed.

Similar as for the specific heat the $T_{\text{max}}(\phi)$ dependence has a pronounced asymmetry in AF and spiral sectors. Denoting again the largest value in each sector by $T_{\text{max}}^*$ we obtain for the triangular lattice

$$T_{\text{max}}(\text{AF})/T_{\text{max}}^* = 1.58$$

which is much larger than the asymmetry value

$$T_{\text{max}}(\text{AF})/T_{\text{max}}^*(\text{CAF}) = 1.11$$

for the square lattice case. Similar to specific heat behavior the $T_{\text{max}}(\phi)$ minimum inside AF and spiral sectors is reached around the most frustrated isotropic triangular position

$$T_{\text{max}}^* \approx 0.35J_c/k_B.$$  

At the one-dimensional point, as for the heat capacity, the results from [26], $k_B T_{\text{max}}/J_c = 0.641$ and

$$\chi(T_{\text{max}})/(N_k \mu_0 (g\mu_B)^2 / J_c) = 0.147$$

are accurately reproduced with our method. In general we think that in particular our results on the magnetic susceptibility can be used to accurately determine both exchange constants $J_1$ and $J_2$ individually, which we show in the following section.

7. Application to Cs$_2$CuCl$_4$ and Cs$_2$CuBr$_4$

As a demonstration of the usefulness of the method, we apply our findings to the compounds Cs$_2$CuCl$_4$ and Cs$_2$CuBr$_4$. Figure 12 shows the temperature dependence of the magnetic susceptibility $\chi(T)$ of Cs$_2$CuCl$_4$ (dots and solid line) and Cs$_2$CuBr$_4$ (open circles and dashed line). The top plot displays the experimental data (symbols, taken from [27]) together with the fits of our FTLM data (lines, fitted values see table 2). The bottom plot displays exactly the same data, this time in dimensionless units using $J_c$, $\phi$, and $g$ for the two compounds from table 2.

Figure 12. Temperature dependence of the magnetic susceptibility $\chi(T)$ of Cs$_2$CuCl$_4$ (dots and solid line) and Cs$_2$CuBr$_4$ (open circles and dashed line). The top plot displays the experimental data (symbols, taken from [27]) together with the fits of our FTLM data (lines, fitted values see table 2). The bottom plot displays exactly the same data, this time in dimensionless units using $J_c$, $\phi$, and $g$ for the two compounds from table 2.
measurement of $\chi(T)$ of Cs$_2$CuCl$_4$ yielded slightly different values [30], however the data analysis was performed over a limited temperature range assuming weakly coupled one-dimensional chains.

As pointed out in section 5.1, the steep decrease of $\chi(T)$ for $T \to 0$ in both cases is an artifact of the finiteness of the tiling used for the FTLM calculations. Assuming a finite-size gap $\Delta \approx J_1/N$, the corresponding temperatures where we expect finite-size effects to dominate are $T_d \approx 0.2$ K for Cs$_2$CuCl$_4$ and $T_d \approx 0.6$ K for Cs$_2$CuBr$_4$. Experimentally, the lowest temperature was $T_{\text{min}} \approx 2$ K, well above the finite-size gaps.

Our result from the FTLM fit to thermodynamic data are compared in table 2 to results from direct spectroscopic methods: INS [28] (Cs$_2$CuCl$_4$ only) and ESR [29], both in fields above the saturation field [2]

$$\mu_0 H_{\text{sat}} = \frac{2S}{g_\mu_B} \left( \frac{J_1 + 2J_2}{2J_2} \right)^2,$$

which is $\mu_0 H_{\text{sat}} \approx 8.4$ T for Cs$_2$CuCl$_4$ and $\mu_0 H_{\text{sat}} \approx 30$ T for Cs$_2$CuBr$_4$. Taking the spectroscopic data at high fields has the advantage that the ground state is fully polarized, corresponding to a single ‘all spins up’ spinor product state [FM]. The excitations on top of this are the N orthonormal single-particle excitations $|\psi_i\rangle = (1/\sqrt{2S}) |S\rangle$ [FM], i.e., $i = 1\ldots N$ with $N = \mathcal{O}(N_c)$. Because $[\mathbf{H}, \mathbf{J}_2] = 0$, the Hamiltonian can not generate more than these one-spin-flip states, and its spectrum can be determined exactly by Fourier transform.

The agreement between the different methods is almost perfect, for exchange parameters as well as g-factors. As already mentioned in [2] if Cs$_2$CuCl$_4$ is interpreted as a purely 2D system this set of exchange parameters puts the compound very close to the quasi-1D spin liquid regime centered at $\phi = 0.5\pi$. In reality, however, the magnetic order is stabilized below $T_{\text{N}} = 0.62$ K by a finite inter-plane coupling of the order $J_{bc} \approx 0.017$ meV along the crystallographic $a$ direction [31].

For Cs$_2$CuBr$_4$, we see deviations of the experimental data from our result at the lowest temperatures. These are not due to impurities [27, 32], but can be regarded as an indication for a tendency towards magnetic order in this compound. The overall energy scale $J_1$ is more than three times larger than for Cs$_2$CuCl$_4$, however the estimate for the anisotropy angle $\phi$ is essentially the same. We therefore expect that Cs$_2$CuBr$_4$ orders magnetically as well, possibly at a higher temperature than its Cl counterpart.

The agreement of our thermodynamic analysis with direct spectroscopic results gives us confidence that the FTL method may be applied to the analysis of the whole Cs$_2$CuCl$_{4-x}$Br$_x$ substitutional series [27, 32].

8. Conclusion and outlook

In this work we have shown that FTLM for finite clusters is a versatile tool to investigate the little known finite temperature properties of frustrated triangular quantum magnets, in contrast to QMC approach which is not suitable in this case. The FTL method complements the analytical spin wave approach which is useful only for the very low temperature regime and is a more straightforward alternative to the high temperature series expansion method.

For this quantum spin model one can use a single control parameter and tune the system through the phase diagram where several special cases with very different frustration degree like frustrated Néel, unfrustrated HAF, frustrated spiral and isotropic triangular 120° phase as well as unfrustrated spin chains and frustrated FM may be realized.

For the largest investigated cluster with $N = 28$ sites we obtain a trustworthy representation of the thermodynamic limit behavior since the exact known result for the spin chain case is produced very well and shows little difference to the $N = 24$ cluster. As a main result we gave the systematic variation of peak position and peak height of specific heat and susceptibility as function of $J_2/J_1$. Both values are strongly suppressed for the most frustrated isotropic triangular magnet (figures 9 and 10). Furthermore a surprisingly large asymmetry in particular for the maximum position exists between the AF and spiral phase region. It is considerably larger than between the AF and CAF regions in the square lattice $J_1$–$J_2$ model. In addition we found that the simple single

| Compound     | Method | $J_1$/meV | $J_2$/meV | $J_3$/meV | $\phi/\pi$ | $g$  | Ref.   |
|--------------|--------|-----------|-----------|-----------|------------|------|-------|
| Cs$_2$CuCl$_4$ | FTLM   | 0.11      | 0.38      | 0.40      | 3.45       | 0.41 | 2.06  | This work |
| INS          | 0.128  | 0.374     | 0.40      | 2.92      | 0.40       | 2.19 | [28]  |
| ESR          | 0.12   | 0.41      | 0.43      | 3.42      | 0.41       | 2.08 | [29]  |
| Cs$_2$CuBr$_4$ | FTLM   | 0.5      | 1.26      | 1.35      | 2.52       | 0.38 | 2.04  | This work |
| ESR          | 0.53   | 1.28      | 1.38      | 2.44      | 0.38       | 2.09 | [29]  |
peak shape of $C_\ell(T)$ and $\chi(T)$ may be distorted due to smaller side maxima or shoulders at lower temperature for some ranges of the control parameter.

The most reliable method to extract the exchange parameters is the fitting of $\chi(T)$ over the whole temperature range (above the finite size gap) using FTM results. We have demonstrated this for two of the typical 2D triangular magnets, $\text{Cs}_2\text{CuCl}_4$ and $\text{Cs}_2\text{CuBr}_4$. We have obtained excellent agreement with results from the INS investigation and with ESR results in the fully polarized state. Our method has the additional advantage that it can easily be extended to the whole substitutional series $\text{Cs}_2\text{CuCl}_4\text{Br}_x(0 \leq x \leq 4)$ [27] to extract the systematic variation of frustration anisotropy control parameter $\phi$ and energy scale $J_t$, as a function of Br concentration [33]. We note that our method can also be applied to magnetocaloric measurements of the organic charge-transfer salts where localized $S = 1/2$ magnetic moments are residing on a possibly distorted triangular lattice as well. This includes the $\text{Et}_4\text{Me}_{4-z}\text{Z}[\text{Pd}((\text{dmit})_2)_2]$ ($x = 0, 1, 2$) family of compounds [34, 35] as well as $\kappa-(\text{ET})_2\text{B}(\text{CN})_4$ and $\kappa-(\text{ET})_2\text{Cu}(\text{CN})_3$ [36] and $\kappa-(\text{BEDT-TTF})_2\text{Cu}[\text{N}(\text{CN})_2]\text{Cl}$ [37].

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