Spin susceptibility of quantum magnets from high to low temperatures.

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We present a method to compute the magnetic susceptibility of spin systems at all temperatures in one and two dimensions. It relies on an approximation of the entropy versus energy (microcanonical potential function) on the whole range of energies. The intrinsic constraints on the entropy function and a careful treatment of boundary behaviors allow to extend the standard high temperature series expansions (HTE) towards zero temperature, overcoming the divergence of truncated HTE. This method is benchmarked against two one-dimensional solvable models: the Ising model in longitudinal field and the XY model in a transverse field. With ten terms in the HTE, we find a spin susceptibility within a few % of the exact results in the whole range of temperature. The method is then applied to two two-dimensional models: the supposed-to-be gapped Heisenberg model and the $J_1$-$J_2$-$J_3$ model on the kagome lattice.

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Recent years have seen an outburst of magnetic materials that might be realistic candidates for the long searched spin liquids¹⁻⁷. In this quickly maturing field, it is now highly desirable to compare the experimental properties of these new states of matter with theory. Modelization of the magnetic interactions in a Mott insulator is a challenge. First principle calculations of the magnetic interactions are delicate⁸⁻⁹. In a pragmatic approach, the experimentally measured specific heat $C_V$ and/or uniform spin susceptibility $\chi$ can be compared against high temperature series expansions (HTE) of spin models. This simple trail is not sufficient for frustrated magnets. In fact HTE diverge at low temperature and increasing the length of the series and/or using Padé approximants do not help much to reach useful information at temperatures much lower than the main interaction. But, as was noticed at the early years of this quest¹⁰, the interesting physics in frustrated systems appear in a range of temperatures at least an order of magnitude lower than the main coupling, and specially for competing interactions where the temperature range available with the raw HTE is quite insufficient.

Faced to this difficulty Roger¹¹ introduced biased differential approximants taking into account the known low temperature algebraic behavior of the Heisenberg magnet on the square and the triangular lattice. This is possible when the nature of the low temperature phase is precisely known, but not for the essentially unknown spin liquids presently under investigation. In ref.¹² a different approach was proposed to extend of the HTE series of the specific heat towards low temperatures, based on the use of two sum rules. However in real materials, phonon and magnetic contributions to the specific heat are often mixed and comparison between specific heat experimental data and models are therefore delicate. On the contrary, the experimental information on the magnetic susceptibility obtained by squid or NMR measurements is free of these uncertainties and it would be extremely valuable to have a way to use all available experimental data. The extension of ref.¹² to spin-susceptibility calculation did not seem a priori possible as its success was thought to be related to the existence of sum rules constraining the specific heat, sum rules which have no equivalent for the spin-susceptibility.

In fact ref.¹² regularization and interpolation procedure is more powerful than expected and it opens the way to computation of all thermodynamic quantities in the whole range of temperatures. The first ingredient of this success comes from the fact that symmetric spin liquids appear in models where we do not expect any phase transitions, i.e. thermodynamic quantities are represented by analytic functions in the whole domain of temperature. The second ingredient comes from the use of the appropriate thermodynamic function for extrapolating the HTE. The major drawback of truncated HTE is the spurious divergence arising in the low temperature free energy: trying to extend its range of validity towards $T=0$ is doomed to failure. The choice to build a reasonable approximation of the entropy versus energy $s(e)$ (the thermodynamic potential of the microcanonical ensemble) is more efficient because: 1- $s(e)$ is defined on the finite interval from the ground state energy $e_0$, to $e_{\infty}$ (the average energy reached by the system for $T$ going to $\infty$), and its boundary values are known: $s(e_0) = 0$ and $s(e_{\infty}) = \ln(2S+1)$. 2- The series expansion of $s(e)$ is exactly known at $e_{\infty}$ from the knowledge of the free energy HTE. The boundary behavior at $e_0$ can be predicted from the qualitative knowledge of the first excitations. 3- In the absence of phase transition (one- or two-dimensional behavior) the function $s(e)$ is a monotonously increasing concave function of $e$. The interpolation of $s(e)$ between $e_0$ and $e_{\infty}$ is thus highly constrained.

In this paper we show that this method allows the construction of the spin susceptibility $\chi$ at all temperatures and non-zero magnetic field. We test this new approach on two cases where the exact $\chi$ is known: the gapped one-dimensional Ising model and the gapless one-dimensional XY-model. Then, we apply it to two open problems: the antiferromagnetic Heisenberg model on the kagome lattice (supposed to be gapped¹³,¹⁴) and the
supposed-to-be gapless cuboc2 spin liquid phase in the $J_1$-$J_2$-$J_4$ model on the same lattice.\textsuperscript{6,15}

We consider a system of $N$ spin-1/2 in a constant magnetic field $B$, $h = mB$ and $m = g\mu_B$. In the following, $h$ will be considered as a parameter. The free energy per spin $f_h$ reads:

$$\beta f_h = \frac{1}{N} \ln \text{Tr} e^{-\beta H_h} \text{ with } \beta = 1/T.$$  \hspace{1cm} (2)

At fixed $h$, the entropy per spin $s_h$ and the energy per spin $e_h$ are given by

$$e_h = f_h - T \frac{\partial f_h}{\partial T} \bigg|_h \text{ and } s_h = - \frac{\partial f_h}{\partial h} \bigg|_h.$$  \hspace{1cm} (3)

From the HTE of $f_h$, the HTE of $e_h$ and $s_h$ are deduced and elimination of $\beta$ between them leads to the series expansion (SE) $s_h^\text{SE}(e)$ of $s_h(e)$ around $e_{\infty}$.

The next step consists to extrapolate $s_h^\text{SE}(e)$ down to $e_{h,0}$. In the absence of a phase transition $s_h(e)$ is indeed analytic on $[e_{h,0}, 0]$, but singular at the boundary $e_{h,0}$, as $s_h'(e) \to \infty$ when $e \to e_{h,0}$ (see Eq.(4)). To account for this singularity, we define a smooth function $G_h(e) = \mathcal{F}(s_h(e), e, e_0)$, where $\mathcal{F}$ is a functional depending on the qualitative nature of the excitation. Then $G_h^\text{SE}(e)$ is calculated from $\mathcal{F}(s_h^\text{SE}(e), e, e_0)$ and transformed into Padé approximants (PA): $G_h^\text{PA}(e)$. Inverting the functional $\mathcal{F}$, we build for each PA a function $s_h^\text{PA}(e)$. We discard all PA’s that do not verify $s_h(e) > 0$, $s_h'(e) > 0$ and $s_h''(e) < 0$. The method is successful when several PA’s coincide for all $e_h \in [e_{h,0}, 0]$.

We then use the microcanonical definition of the temperature:

$$s_h'(e) = \frac{\partial s_h(e)}{\partial e} \bigg|_h = \beta = \frac{1}{T},$$  \hspace{1cm} (4)

to compute $e_h(\beta)$ from $s_h^\text{PA}(e)$ and $f_h^\text{PA}(\beta) = e_h(\beta) - Ts_h^\text{PA}(e_h(\beta))$ for the evaluation of the magnetic susceptibility per spin:

$$\chi = - \frac{\partial^2 f_h}{\partial \beta^2} \bigg|_T = -m^2 \frac{\partial^2 f_h}{\partial h^2} \bigg|_T.$$  \hspace{1cm} (5)

Thermodynamic functions are even in $h$, thus the second derivative of $f_h(\beta)$ at $h = 0$ is evaluated by finite differences using the same PA as

$$\chi^\text{PA}(\beta, h = 0) \simeq - \frac{2}{\partial h^2} \left( f_h^\text{PA}(\beta) - f_0^\text{PA}(\beta) \right),$$  \hspace{1cm} (6)

and similarly at $h \neq 0$.

**Gapped systems: the longitudinal spin susceptibility of the 1D-Ising model.**

The Hamiltonian is $\mathcal{H}_0 = \sum_i 2S_{i,z}S_{i+1,z}$. For $h$ smaller than the gap, the ground state energy $e_0$ is independent of $h$ ($\chi(T = 0) = -m^2 \partial^2 e/\partial h^2|_{T = 0}$). Around $e_0$, the singularity of $s_h(e)$ takes the form $- (e - e_0) \ln(e - e_0)/\Delta_h$, where $\Delta_h$ is the gap. To account for this behavior we use the functional:

$$\mathcal{F}(s_h, e, e_0) = (e - e_0) \frac{d s_h(e)}{d e}.$$  \hspace{1cm} (7)

Using the exact value $e_0(h) = -1/2$, and an HTE at order 4 only, $\chi$ is already reproduced within 1%. Increasing the order of the series decreases both the maximum error and the range of temperature where the errors are non negligible.

As in most cases $e_0(h)$ is unknown, we now consider it as a free parameter, here independent of $h$. $e_0$ is adjusted by maximizing the number of $s_h^\text{PA}(e)$, this criterion is very accurate and gives $e_0 \in [-1/2 - 10^{-9}, -1/2 + 10^{-7}]$. The error on $\chi$ for the 12-order series is less than $2 \times 10^{-3}$ (see Fig.1), and we find a gap to be the exact value 1, within an error of $10^{-9}$.

**Gapless model: the transverse spin susceptibility of the 1d XY-model.**

The Hamiltonian reads $\mathcal{H}_0 = \sum_i 2(S_{i,x}S_{i+1,x} + S_{i,y}S_{i+1,y})$. Exact results have been obtained by Katsura.\textsuperscript{16} The specific heat is linear in $T$ at low temperature, thus the singularity of $s_h(e)$ around $e_{h,0}$ takes the form $s_h(e) \propto \sqrt{e - e_{h,0}}$. It is taken into account by

$$\mathcal{F}(s_h, e, e_{h,0}) = \frac{s(e)^2}{e - e_{h,0}}.$$  \hspace{1cm} (8)

Using the exact value of $e_{h,0}$ leads to the exact value of $\chi(T = 0)$ and values of $\chi$ within an error of less than 1% in the whole range of temperature for a 12-term series. Leaving $e_{h,0}$ as a free parameter, the errors do not exceed a few percents in the whole range of temperature (see Fig.2).
Antiferromagnetic Heisenberg model on the kagome lattice.

The spin-1/2 antiferromagnetic Heisenberg model on the kagome lattice, \( \mathcal{H}_0 = \sum_{\langle i,j \rangle} \mathbf{S}_i \cdot \mathbf{S}_j \), is a quintessential example of the effects of both geometric frustration and quantum fluctuations pushed to their limit. The infinite degeneracy of the classical ground-state is transferred in the quantum case to a very large density of low lying excitations, which makes the problem very difficult. After many studies, decisive progresses in 2D DMRG have ascertain the value of the ground-state energy of this system, \( e_0 = -0.4386(5) \), and estimate the spin gap of the order of 0.13(1).\(^{13,14}\) Early HTE of Eltsner et Young\(^{17}\), extended in this work to order 17 give a first idea of the HT behavior of the thermodynamical quantities. The HTE diverges around \( T = 1 \) and the Padé approximant below \( T = 0.4 \) (see Fig.3).

With the hypothesis of a gapped system, \( G(e,h) \) is built using Eq.(7). Results displayed in Fig.3 are obtained by fixing \( e_0 \) to its best known value (\( e_0 = -0.4386 \)) (red curve) and to two extreme values which differ by 5 standard deviations from the the present best DMRG estimate. For a given value of \( e_0 \), the differences between the various \( \chi^\text{PA} \) are less than the thickness of the lines. For this range of ground state energies, we find a gap 0.03(1), significantly smaller than the gap obtained in the DMRG approach. Compared to exact diagonalisations (ED) on 18 and 24-spin samples\(^{17,18}\), we find, at the thermodynamic limit, a smaller value for the maximum of \( \chi \) (~0.12). In ED, the spin-spin correlations are indeed overemphasized by the very small lengths of the samples. The existence of a low temperature shoulder in the specific heat is confirmed. Unfortunately, comparison with experimental date of Herbertsmithite cannot be done because of sizable Dzyaloshinskii-Moriya interactions that change the low energy spectrum of excitations and probably close the gap.\(^{19,20}\)

Spin susceptibility of Kapellasite.

This material is in a Mott phase and its properties is analyzed using a spin-1/2 Hamiltonian on the kagome lattice.\(^6,15\)

\[ \mathcal{H}_0 = J_1 \sum_{\langle i,j \rangle} \mathbf{S}_i \cdot \mathbf{S}_j + J_2 \sum_{\langle\langle i,j \rangle\rangle} \mathbf{S}_i \cdot \mathbf{S}_j + J_d \sum_{\langle\langle\langle i,j \rangle\rangle\rangle} \mathbf{S}_i \cdot \mathbf{S}_j \]  

(9)

where \( J_d \) is the third-neighbor exchange interaction across the hexagon. The best set of parameters, obtained from a fit of the spin susceptibility down to \( T = 17.5K \), reads \( J_1 = -12K \), \( J_2 = -4K \), and \( J_d = 15.6K \).\(^{15}\) The breakthrough of the present work allows the computation of the spin susceptibility down to \( T = 0 \). From a low-temperature specific heat \( \propto T^2 \), the singularity of \( s_h(e) \) around \( e_{h,0} \) takes the form \( s_h(e) \propto (e - e_{h,0})^{2/3} \). It is taken into account by

\[ F(s_h, e, e_{h,0}) = \frac{s(e)^{3/2}}{e - e_{h,0}} \]  

(10)

with adjusted \( e_{h,0} \).\(^{15}\)

The full curves of Fig.4 are obtained for the above-mentioned best set. As expected they indeed agree with

FIG. 2. (Color online) Same as Fig.1 for the transverse spin susceptibility of 1D-XY model, where \( e_0(h) \) is left free to adjust.

FIG. 3. (Color online) Spin susceptibility \( \chi \) and specific heat \( C_v \) of the antiferromagnetic Heisenberg model on the kagome lattice. Shown in the figures are the HT series expansion to order 17 (green dotted lines), the best Padé approximant of this simple series (magenta dotted line), and the results of the present interpolation (full lines). The sensitivity of the interpolation to the ground-state energy \( e_0 \) is displayed on both quantities. The full red curves are associated to the best commonly admitted value of \( e_0 \) (see text).
experiments down to 17.5K. We see an increasing disagreement with experimental data when going to lower temperatures. Part of the disagreement can be assigned to the magnetic field, which has a large effect in this system with competing interactions (Fig. 4). Up to now, the HTE for this model are available to order 4 in $h$ only, which limits the evaluation of $\chi(h)$ to $h/|J_1| \lesssim 0.25$, that is a magnetic field less than 3 Tesla, while experimental data are at 5 Tesla. Nevertheless, with a small change of the coupling constants $J_1 = -12$ K, $J_2 = -5.2$ K and $J_d = 16.4$ K, and 3 Tesla magnetic field, we can fit almost all experimental data. A small disagreement persists at the lowest temperature, where the magnetic field effects are the most important. The uncertainties on the set of parameters is considerably reduced with this present method because we use experimental data at all temperatures and include the effect of the magnetic field. For Kapellasite, experimental data at lower field and/or longer series in $h$ will help to achieve a better determination of the parameters.

In this paper we have proposed a method to extend the HTE of the spin susceptibility down to $T = 0$, based on a reconstruction of the entropy versus energy per spin. We have checked the method against gapless and gapped exact models: the largest deviations from the exact results are of the order of $10^{-2}$ or better with an original HT series expansion of ten terms. We have applied this method to open problems on the kagome lattice. Being not limited by finite size effects, we believe in the accuracy of the present method compared to that of exact diagonalisations, specially at low temperature. We have equally shown that this approach can be used to compute the spin susceptibility in a finite magnetic field, which is a major point for the comparison between models and experimental squid data. In principle, this method can be used for the calculation of all response functions of lattice problems. We believe that such an approach could be successfully applied to any of the spin liquid compounds already discovered improving the analysis of these states of matter and comparison with theories.

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