Spin Susceptibility of Quantum Magnets from High to Low Temperatures

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(Received 3 July 2014; published 4 February 2015)

We explain how and why all thermodynamic properties of spin systems can be computed in one and two dimensions in the whole range of temperatures overcoming the divergence towards zero temperature of the standard high-temperature series expansions (HTEs). The method relies on an approximation of the entropy versus energy (microcanonical potential function) on the whole range of energies. The success is related to the intrinsic physical constraints on the entropy function and a careful treatment of the boundary behaviors. 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 percent of the exact results over the entire range of temperatures. The method is then applied to two two-dimensional models: the supposedly gapped Heisenberg model and the J_1-J_2-J_d model on the kagome lattice.

DOI: 10.1103/PhysRevLett.114.057201 PACS numbers: 75.10.Jm, 02.60.Ed, 05.70.-a, 75.40.Cx

Recent years have seen the development of a plethora of magnetic materials that might be realistic candidates for the long-sought spin liquids [1–8]. 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 particularly challenging, and first principles calculations of the magnetic interactions are delicate [9,10]. In a pragmatic approach, the experimentally measured specific heat C_V and/or uniform spin susceptibility $\mathcal{X}$ can be compared to high-temperature series expansions (HTEs) of spin models [11]. This simple method, however, is not sufficient for frustrated magnets due to divergence at low temperatures, and increasing the length of the HTE series and/or using Padé approximants do not help much to obtain useful information at temperatures lower than the main interaction. But, as was noticed during the early years of this quest [12], the interesting physics in frustrated systems appears in a range of temperatures at least an order of magnitude lower than the main coupling and particularly for competing interactions where the temperature range available with the raw HTE is insufficient.

Many mathematical methods have been tried to obtain low-temperature properties of magnets. For example, biased differential approximants have been successful to account for the Néel ground states of the Heisenberg model on the square and the triangular lattice [13]. For the spin liquids presently under investigation, other tools are needed. In Refs. [14,15], a different approach based on the use of sum rules was proposed to compute specific heat at zero magnetic field. Unfortunately, in real materials, phonon and magnetic contributions to the specific heat are often mixed and extracting the magnetic contribution is delicate. On the other hand, 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 it. The extension of the method presented in Refs. [14,15] 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 do not have an equivalent for the spin susceptibility.

In fact, deep physical reasons imply that the regularization and interpolation procedure of Refs. [14,15] is more powerful than expected. From a conceptual point of view, the first key point is the move from an expansion of the free energy f as a function of the temperature T, to an expansion of the entropy s as a function of the internal energy e. Elementary statistical mechanics tells us that these two descriptions (canonical versus microcanonical ensembles) are, indeed, equivalent and that all thermodynamic quantities can be computed in the thermodynamic limit in either of them. The major drawback of the standard use of the truncated HTE is the intrinsic divergence arising in the low-temperature free energy: trying to extend its range of validity towards $T = 0$ is, thus, extremely difficult. The choice to build a reasonable approximation of the entropy versus energy $s(e)$ [and by extension of $s(e, h)$, where h is the external magnetic field] is more efficient because of the following. (i) $s(e)$ is defined on the finite interval from the ground-state energy e_0 to e_∞ (the average energy reached by the system for $T \to \infty$), and its boundary values are known: $s(e_0) = 0$ and $s(e_\infty) = \ln(2S + 1)$. (ii) The series expansion of $s(e)$ at e_∞ can be exactly deduced from the free energy HTE. (iii) In the absence of a phase transition (one- or two-dimensional behavior), the function $s(e)$ is an infinitely differentiable function on $]e_0, e_\infty]$, monotonically increasing $[s'(e) = 1/T > 0]$ and concave [second derivatives of $s(e, h)$ negative because of the stability conditions of the thermodynamical equilibrium]. (iv) The correct

behavior of $s'(e)$ at e_0 can be determined from a qualitative knowledge (or prediction) of the first excitations (see below). The interpolation of $s(e)$ between e_0 and e_∞ is, thus, very strongly constrained by physical considerations. All these thermodynamic conditions exist in the canonical ensemble, and they should equally constrain physical expansions of the free energy versus temperature and their extrapolation. Their implementation in the computation is never done (it would be difficult, if not impossible to do [16]), whereas it is very simple in the present approach.

In this Letter, we show that this approach in the microcanonical ensemble allows the construction of $s(e,h)$ and as a consequence of all thermodynamic properties at all temperatures in zero and moderate magnetic fields. We concentrate on the spin susceptibility $\mathcal{X}(T)$ and test the method on two cases where the exact function is known: the gapped one-dimensional Ising model and the gapless one-dimensional XY model. Then, we address two open problems: the antiferromagnetic Heisenberg model on the kagome lattice (supposed to be gapped [17,18]) and the supposedly gapless cuboc2 spin liquid phase in the J_1-J_2-J_d model on the same lattice [6,19].

We consider a system of N spin-1/2 in a constant magnetic field B in the z direction. The Hamiltonian reads

$$\mathcal{H}_h = \mathcal{H}_0 - hS_z, \tag{1}$$

where $\mathcal{H}_0$ is a spin Hamiltonian, S_z is the total spin along 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

$$\beta f_h = -\frac{1}{N}\ln \mathrm{Tr} e^{-\beta\mathcal{H}_h} \quad \text{with} \quad \beta = 1/T. \tag{2}$$

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

$$e_h = f_h - T\left.\frac{\partial f_h}{\partial T}\right|_h \quad \text{and} \quad s_h = -\left.\frac{\partial f_h}{\partial T}\right|_h. \tag{3}$$

From the series expansion of $f(T,h)$ in T and h, we first compute the HT series of f_h at fixed h, and from now, each function is evaluated at this h. The HT series e_h and s_h are deduced, and the elimination of β between them leads to the series expansion (SE) $s_h^{\mathrm{SE}}(e)$ of $s_h(e)$ around e_∞ (see the Supplemental Material [20]).

The next step consists of extrapolating $s_h^{\mathrm{SE}}(e)$ 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 $s_h'(e) = 1/T \to \infty$, when $e \to e_{h,0}$. The key point introduced in Refs. [14,15] is then to build from $s_h(e)$ a function $G_h(e)$ defined on $[e_{h,0}, e_\infty]$ removing this singularity. This can be achieved by noting that two main kinds of leading singularities are met. If the system is gapless with a specific heat $C_v(T)_{T\to 0} \propto T^\alpha$, then $s_h(e \to e_{h,0}) \propto (e - e_{h,0})^{(\alpha/(\alpha+1))}$, and we choose

$$G_h(e) = \frac{s_h(e)^{(1+1/\alpha)}}{e - e_{h,0}}. \tag{4}$$

If the system is gapped, with $C(T) \propto (1/T^2)e^{\Delta_h/T}$, then the singularity of $s_h(e \to e_{h,0}) \propto -(e - e_{h,0})\ln(e - e_{h,0})/\Delta_h$, and we can choose

$$G_h(e) = (e - e_{h,0})\left(\frac{s_h(e)}{e - e_{h,0}}\right)', \tag{5}$$

where the $'$ denotes the differentiation with respect to e. $G_h(e)$ is a smooth function on $[e_{h,0}, e_\infty]$ that is easy to extrapolate. This is done as follows: from the series expansion of $s_h^{\mathrm{SE}}(e)$ at e_∞, we deduce the series expansion of $G_h^{\mathrm{SE}}(e)$ and build the Padé approximants (PA) $G_h^{\mathrm{PA}}(e)$. The inversion of Eq. (4) or (5) gives for each PA a function $s_h^{\mathrm{PA}}(e)$ [21]. By construction, this method preserves both the exact information coming from the high-temperature series and the supposed-to-be correct behavior at $e_{h,0}$. At this stage, any unphysical PA, i.e., one not verifying $s_h(e) > 0$, $s_h'(e) > 0$ and $s_h''(e) < 0$, is discarded. The method is considered successful when most of the physical PAs coincide for $e \in [e_{h,0}, 0]$. This criterion is a way to select the most robust approximation and extract the most plausible information from the restricted amount of data: it is a soft measurement of the self-consistency of this approach (see Ref. [15], for example). Heuristically, we noticed that spoiling the appropriate regularization at $e_{h,0}$ (i.e., shifting slightly its value or changing α) prevents one from obtaining many coincident PAs and gives erratic results when increasing the length of the input HT series.

In order to evaluate the magnetic susceptibility $\mathcal{X}(T)$, we need $f_h(T)$. Using $s_h'(e) = 1/T = \beta$, we compute $e_h(\beta)$ from $s_h^{\mathrm{PA}}(e)$ and $f_h^{\mathrm{PA}}(\beta) = e_h(\beta) - Ts_h^{\mathrm{PA}}[e_h(\beta)]$. $\mathcal{X}$ is given by

$$\mathcal{X} = -\left.\frac{\partial^2 f_h}{\partial B^2}\right|_T = -m^2\left.\frac{\partial^2 f_h}{\partial h^2}\right|_T, \tag{6}$$

where the second derivative of f_h with respect to h is obtained by finite differences of the same PA at different h. The results presented here have been obtained from a series expansion of $f(T,h)$ at order 4 in h, which limits the range of applicability to small magnetic fields (not a conceptual limit, just a current technical one).

Gapped systems: The longitudinal spin susceptibility of the 1D Ising model at $h = 0$.— The Hamiltonian is $\mathcal{H}_0 = \sum_i 2S_{i,z}S_{i+1,z}$. We use the regularizing function defined in Eq. (5). With the exact value $e_0(h) = -1/2$ and a HTE at order 4 only, $\mathcal{X}$ is already reproduced within 1%. Increasing the order of the series decreases both the

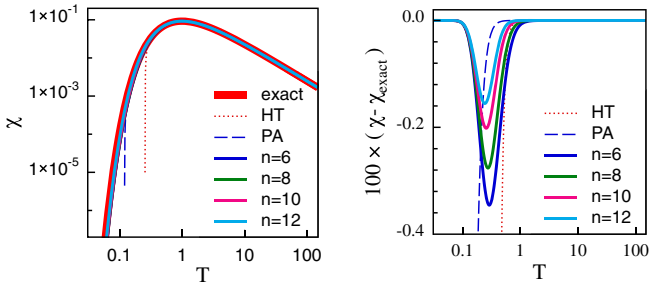

FIG. 1 (color online). Comparison between the present method and exact results for the longitudinal spin susceptibility of the 1D Ising model. Left: Our results compared to the exact solution. Right: Differences between exact $\mathcal{X}$ and the various approximations. HT (dotted line) stands for the HTE at order 12; PA (dashed line) stands for the [6-6] Padé approximant; the other curves stand for the present method using HTE at various order n.

maximum error and the range of temperatures where the errors are non-negligible.

As in most cases the ground state energy EG is not known, we have also considered it as a free parameter to check the method. e_0 is then adjusted by maximizing the number of $s_h^{\mathrm{PA}}(e)$. This criterion is very accurate and gives $e_0 \in [-1/2 - 10^{-9}, -1/2 + 10^{-7}]$. The error on $\mathcal{X}$ for the 12-order HT series is less than 2×10^{-3} (see Fig. 1), and we find a gap 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 [22]. The specific heat is linear in T at low temperatures; thus, the singularity of $s_h(e)$ around $e_{h,0}$ is regularized through Eq. (4). Using the exact value of $e_{h,0}$ leads to the exact value of $\mathcal{X}(T=0)$ and values of $\mathcal{X}$ within an error of less than 1% in the whole range of temperatures for a 12-term HT series. Leaving $e_{h,0}$ as a free parameter, the errors never exceed a few percent in the whole range of temperatures (see Fig. 2).

Antiferromagnetic Heisenberg model on the kagome lattice.—The spin-1/2 antiferromagnetic Heisenberg model on the kagome lattice $\mathcal{H}_0 = \sum_{<i,j>} \mathbf{S}_i.\mathbf{S}_j$ is a quintessential example of the effects of both geometric

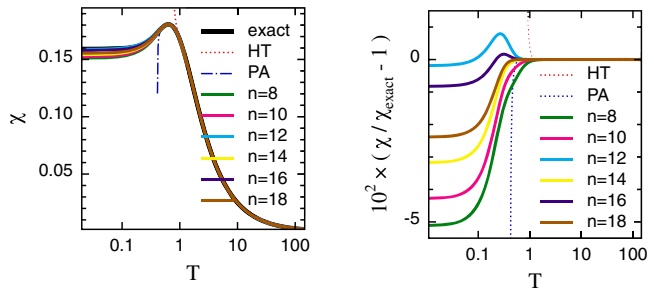

FIG. 2 (color online). Same as Fig. 1 for the transverse spin susceptibility of the 1D XY model, where EG is left free to adjust.

frustration and quantum fluctuations pushed to their limit. After much effort, decisive progress in 2D density matrix renormalization group (DMRG) has led to the value of the ground-state energy of this system $e_0 = -0.4386(5)$ and an estimate the spin gap of the order of 0.13(1) [17,18]. The early HTE of Elstner and Young [23] extended in this work to order 17 gives a first idea of the HT behavior of the thermodynamical quantities. The HTE diverges around $T = 1$, and the Padé approximants of this series diverge below $T = 0.4$ (see Fig. 3).

With the hypothesis of a gapped system, $G(e, h)$ is built using Eq. (5). The results displayed in Fig. 3 were 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 present best DMRG estimate. For a given value of e_0, the differences between the various $\mathcal{X}^{\mathrm{PA}}$ 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.

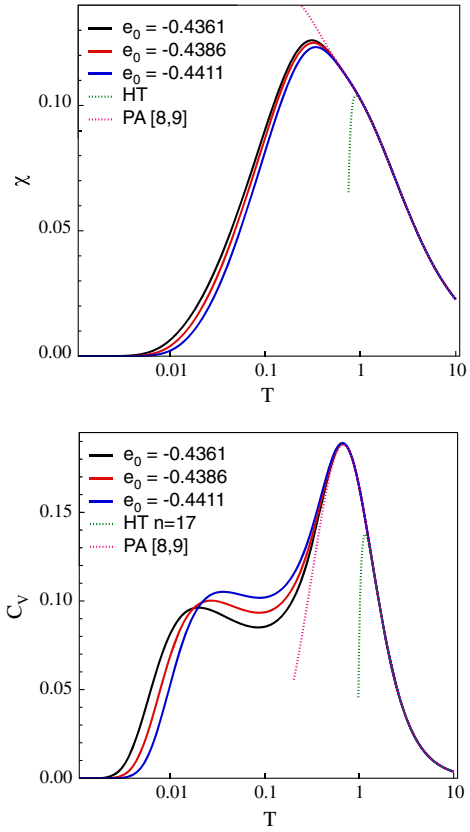

FIG. 3 (color online). Spin susceptibility χ and specific heat C_v of the antiferromagnetic Heisenberg model on the kagome lattice. Shown in the figures are the HT series expansion to order 17 (green dotted lines), the best Padé approximant of this simple series (magenta dotted line), and the results 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 with the best commonly accepted value of e_0 (see text).

Compared to exact diagonalizations (EDs) on 18- and 24-spin samples [23,24], we find, in the thermodynamic limit, a smaller value for the maximum of $\mathcal{X}$ ($\sim$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, it proved impossible to compare with the experimental data of herbertsmithite due to sizable Dzyaloshinskii-Moriya interactions that change the low energy spectrum of excitations and probably close the gap [25,26].

Spin susceptibility of kapellasite. This material is in a Mott phase, and its properties are analyzed using a spin-1/2 Hamiltonian on the kagome lattice [6,19]:

$$\mathcal{H}_0 = J_1 \sum_{\langle i,j \rangle} \mathbf{S}_i.\mathbf{S}_j + J_2 \sum_{\langle\langle i,j \rangle\rangle} \mathbf{S}_i.\mathbf{S}_j + J_d \sum_{\langle\langle\langle i,j \rangle\rangle\rangle} \mathbf{S}_i.\mathbf{S}_j, \quad (7)$$

where J_d is the third-neighbor exchange energy across the hexagon. The best set of parameters obtained from a fit of the spin susceptibility down to $T = 17.5$ K, reads $J_1 = -12$ K, $J_2 = -4$ K, and $J_d = 15.6$ K [19]. The low-temperature specific heat is experimentally known to be $\propto T^2$; we then use Eq. (4) to regularize $s(e)$ and adjust $e_{h,0}$. The full curves of Fig. 4 are obtained for the above-mentioned best set. As expected, they agree with experiments down to 17.5 K. We see an increasing disagreement with experimental data when going to lower temperatures. Part of the disagreement can be attributed to the magnetic field, which has a large effect in this system with competing interactions (Fig. 4). Up to now, the HTEs for this model are available to order 4 in h only, which limits the evaluation of $\mathcal{X}(h)$ to $h/|J| \lesssim 0.25$, i.e., a magnetic field of less than 3 T, while experimental data are at 5 T. Nevertheless, with a small change of the coupling constants, namely, $J_1 = -12$ K, $J_2 = -5.2$ K, and $J_d = 16.4$ K, and 3 T 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 in the parameter set are considerably reduced with the 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 lead to a better determination of the parameters.

In this Letter, 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 diagonalizations,

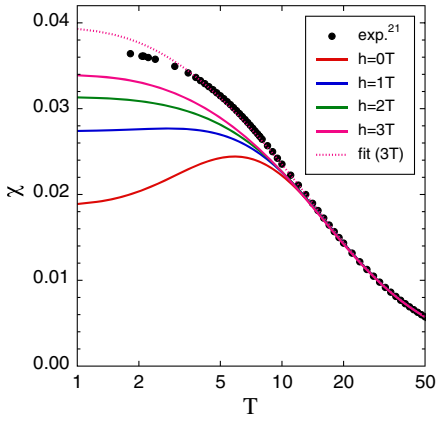

FIG. 4 (color online). Spin susceptibility comparison between experiment [27] at 5 T and the J_1-J_2-J_d model for different values of the magnetic field 0, 1, 2, 3 T with $J_i(K) = [-12, -4, 15.6]$ and the new fit (see text).

especially at low temperatures. We have also shown that this approach can be used to compute the spin susceptibility in a finite magnetic field, which allows a comparison between models and experimental squid data [20]. The method is general in its principle and can be applied straightforwardly to other models, whatever the size of the spin, as long as the high-temperature expansion of the free energy per spin is available [11]. This opens a large range of interesting studies such as the application of the Heisenberg model with Dzaloshinskyi-Moryia interactions to herbertsmithite, with spatially anisotropic couplings to volborthite [1–8]. A further conceptual question has not been studied in the present work: is this approach able to deal with critical phase transitions? This might be possible for temperatures larger than T_c in as much as the correct diverging behavior at T_c is taken into account, but this is probably more delicate than the present work as these divergences are singularities in the derivatives of $s(e)$ (see the Supplemental Material [20]). Building of a suitable regularization function and benchmarking the method is a new subject in itself, beyond the scope of this Letter.

We thank G. Misguich for fruitful discussions and Julian Talbot for a critical reading of the manuscript. We acknowledge the support of the French ministry of research through the ANR grant "SpinLiq."

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