Thermodynamics of quantum Heisenberg spin chains

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Thermodynamic properties of the quantum Heisenberg spin chains with \( S = 1/2, 1, \) and \( 3/2 \) are investigated using the transfer-matrix renormalization-group method. The temperature dependence of the magnetization, susceptibility, specific heat, spin-spin correlation length, and several other physical quantities in a zero or finite applied field are calculated and compared. Our data agree well with the Bethe ansatz, exact diagonalization, and quantum Monte Carlo results and provide further insight into the quantum effects in the antiferromagnetic Heisenberg spin chains.

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I. INTRODUCTION

There are a lot of quasi-one dimensional compounds whose behaviors can be adequately described within the framework of interacting spin chains governed by the Heisenberg model. Extensive studies on this model have shed light on the quantum nature of spin dynamics. In 1983, Haldane predicted that the one-dimensional Heisenberg antiferromagnetic model with integer spin has an excitation gap and a finite correlation length \[ 6 \]. Since then a great amount of experimental and theoretical effort has been made towards understanding the difference between half-integer and integer spin chains.

In this paper we report results of a transfer-matrix renormalization-group (TMRG) \[ 2–4 \] study for the thermodynamics of quantum Heisenberg spin chains. We have calculated the magnetic susceptibility, specific heat, spin-spin correlation length, and other experimentally relevant quantities as functions of temperature and applied magnetic field for the \( S=1/2, 1, \) and \( 3/2 \) spin chains.

The Heisenberg model is defined by the Hamiltonian

\[
\hat{H} = \sum_{i}^{N} h_{i}; \quad h_{i} = JS_{i} \cdot S_{i+1} - \frac{H}{2}(S_{iz} + S_{i+1z}),
\]

where \( J \) is the spin exchange constant and \( H \) is an applied magnetic field \[ 5 \]. In this paper, we consider antiferromagnetic spin chains only. We use units in which \( J = 1 \).

The spin-1/2 Heisenberg model is integrable by Bethe ansatz. Many of its thermodynamic quantities, for example, the specific heat and the spin susceptibility, can be calculated by solving the Bethe ansatz equations. The conformal field theory is also very useful in analysing the low temperature low field thermodynamic properties, since the \( S=1/2 \) Heisenberg model is equivalent to the \( k=1 \) Wess-Zumino-Witten nonlinear \( \sigma \) model.

Higher spin Heisenberg models are not at present amenable to rigorous solution. The finite temperature properties of the model were studied mainly through transfer matrix \[ 6 \], quantum Monte Carlo \[ 7–9 \], and other approximate methods \[ 10,11 \].

At zero field, the ground state of \( \hat{H} \) is a spin singlet with zero spin magnetization. At finite field, the magnetization of the ground state becomes finite and increases with increasing \( H \). There is a critical field \( H_{c2} \) beyond which all spins are fully polarized at zero temperature. If we denote \( E(N,S) \) as the lowest eigenvalue of a \( N \)-site Heisenberg chain with total spin \( S \) at \( H = 0 \), then it is straightforward to show that \( H_{c2} = E(N,S_{\text{max}}) - E(N,S_{\text{max}} - 1) = 4S \), independent on \( N \).

Below \( H_{c2} \), a canted Neel order, namely a state which has both ferromagnetic order along the z-axis and antiferromagnetic order in the xy plane, exists at sufficiently low temperature, and the pitch vector (i.e. the value of the momenta at which the static structure factor shows a peak) decreases continuously from \( \pi \) to \( 0 \) with increasing \( H \).

Integer spin chains can be described by the quantum nonlinear \( \sigma \) model. It is from the study of this model that Haldane made the famous 'Haldane conjecture'. The ground state of the \( O(3) \) \( \sigma \) model has a finite excitation gap and consequently a finite correlation length. The application of a magnetic field causes a Zeeman splitting of the triplet with one member crossing the ground state at \( \Delta \). When \( H < H_{c1} \), the Haldane gap persists and the ground state is still a non-degenerate spin singlet state. When \( H_{c1} < H < H_{c2} \), the ground state has a nonzero magnetization with gapless excitations. Thus across \( H_{c1} \), an integer spin system undergoes a commensurate to incommensurate transition. This is an interesting feature which is absent in a half odd integer spin system. Evidence for such transitions has been used to identify the Haldane gap in NENP \[ 12 \] and other quasi-1d spin compounds \[ 13 \]. Just above \( H_{c1} \), the ground state can be regarded as a Bose condensate of the low energy boson. Varying the magnetic field is equivalent to varying the chemical potential for this boson and the (uniform) magnetization corresponds to the boson number \[ 14 \].
II. TMRG

In this section, we discuss briefly the TMRG method. A more detailed introduction to the method can be found from Refs. [3,4].

The TMRG method starts by mapping a 1d quantum system onto a 2d classical one with the Trotter-Suzuki decomposition and represents the partition function as a trace of a power function of virtual transfer matrix $T_M$:

$$ Z = \text{Tr} e^{-\beta H} = \lim_{M \to \infty} \text{Tr} T_M^{N/2}, $$

where $M$ is the Trotter number. $T_M$ is defined by an inner product of $2M$ local transfer matrices

$$ \langle \sigma_1^1 \ldots \sigma_{2M}^1 | T_M | \sigma_1^2 \ldots \sigma_{2M}^2 \rangle = \sum_{k=1}^{M} \prod_{m=1}^{M} t(\sigma_1^m \sigma_{m+1}^m | \sigma_1^m \sigma_{m+1}^m) t(\sigma_1^m \sigma_{m+1}^m | \sigma_1^1 \sigma_{2}^3), $$

where

$$ t(\sigma_1^m \sigma_{m+1}^m | \sigma_1^m \sigma_{m+1}^m) = (-\sigma_1^m, \sigma_{m+1}^m | e^{-\tau h} | \sigma_1^m, -\sigma_{m+1}^m) $$

and $\tau = \beta/M$. $| \sigma_1^m \rangle$ is an eigenstate of $S_i^z$ and $\sigma_1^m$ is the corresponding eigenvalue: $S_i^z | \sigma_1^m \rangle = \sigma_1^m | \sigma_1^m \rangle$. The superscripts and subscripts in $T_M$ represent the spin positions in the Trotter and real space, respectively.

$T_M$ conserves the total spin in the Trotter space, i.e. $\sum_k \sigma_1^k$. Thus $T_M$ is block diagonal according to the value of $\sum_k \sigma_1^k$. For the $S=1/2$ Heisenberg model, it was shown rigorously that the maximum eigenstate of $T_M$ is non-degenerate and in the subspace $\sum_k \sigma_1^k = 0$ subspace, irrespective of the sign of $J$ and the value of $H$ [3,4]. When $S > 1/2$, we found numerically that the maximum eigenvectors of $T_M$ are also in the $\sum_k \sigma_1^k = 0$ subblock.

In the thermodynamic limit, the free energy per spin, is given by

$$ F = -\lim_{N \to \infty} \frac{1}{N} \beta \ln Z = -\frac{1}{2\beta} \lim_{M \to \infty} \ln \lambda_{max}, $$

where $\lambda_{max}$ is the maximum eigenvalue of $T_M$. From the derivatives of $F$ one can in principle calculate all thermodynamic quantities. The internal energy $U$ and the spin magnetization $M_z$ could, for example, be calculated from the first derivative of $F$ with respect to $H$ and $T$, respectively. However, numerically it is better to calculate $U$ and $M_z$ directly from the eigenvectors of $T_M$ [3].

The spin susceptibility $\chi = \partial M_z / \partial H$ and the specific heat $C = \partial U / \partial T$ can then be calculated by numerical derivatives. The specific heat such determined is generally found to be less accurate than, for example, the susceptibility data at low $T$. The reason for this is that $U$ changes very slowly with $T$ (or equivalently $C$ is very small) at low $T$, and a small error in $U$ would lead to a relative large error in $C$.

The correlation length of the spin-spin correlation functions, defined by $\xi^{-1} = -\lim_{L \to \infty} \ln \langle S_{i}^z, S_{i+L}^z \rangle$, can also be calculated from this method. The longitudinal and transverse correlation lengths are determined by

$$ \xi_z^{-1} = \frac{1}{2} \lim_{M \to \infty} \ln \frac{\lambda_{max}}{\lambda_2}, \quad (4) $$

$$ \xi_x^{-1} = \frac{1}{2} \lim_{M \to \infty} \ln \frac{\lambda_{max}}{\lambda_1}, \quad (5) $$

where $\lambda_2$ is the second largest eigenvalue of $T_M$ in the subspace $\sum_k \sigma_1^k = 0$ and $\lambda_1$ is the largest eigenvalue of $T_M$ in the subspace $\sum_k \sigma_1^k = \pm 1$.

Figure 1 shows the configuration of superblock used in our calculation. This configuration of superblock is different from those used in Refs. [3,4]. The advantage for forming the superblock in such a way is that the transfer matrix $T_M$ in this case can always be factorized as a product of two sparse matrices (which are block diagonal with respect to $n_s$ and $\sigma_3 \otimes n_e$, respectively). To treat these two sparse matrices instead of $T_M$ itself allows us to save both computer memory space and CPU time.

We compute the maximum eigenvalue, $\lambda_{max}$, and the corresponding right and left eigenvectors, $| \psi^R \rangle$ and $| \psi^L \rangle$, of $T_M$ using an implicitly restarted Arnoldi method [4]. This method is more efficient than the power method which we used before [3,4]. $\lambda_{1,2}$ can also be calculated from this method, but their truncation errors are generally larger than those of $\lambda_{max}$. Thus the correlation lengths determined from Eqs. (4,5) are generally expected to be less accurate than the free energy or other thermodynamic quantities.

In the TMRG method, the density matrix for the augmented system or environment block is non-symmetric, which is different than in the zero-temperature DMRG method. Numerically it is much more difficult to treat
accurately a nonsymmetric matrix than a symmetric one because the errors in \(|\psi^H|\) and \(|\psi^L|\) may affect the the (semi-) positiveness of the density matrix and increase the truncation error of the TMRG.

The TMRG treats directly an infinity spin chain. There is therefore no finite size effect. The error caused by the finiteness of the Trotter number (or \(\tau\)) is of order \(\tau^2\), which is generally very small. The error resulted from the truncation of basis states is difficult to estimate. A rough estimation for this type of error can be obtained from the value of truncation error, which is smaller than \(10^{-3}\) in all our calculations. More accurate results can be obtained simply by extrapolating the results with respect to both \(\tau\) and the number of states retained \(m\).

III. RESULTS

A. S=1/2

The S=1/2 Heisenberg model is by far the best understood spin system. In the absence of field, the ground state is massless and the Bethe ansatz result for the ground state energy is \((1/4 - \ln 2)\). The lowest excitations states are spin triplets with a spin wave spectrum \(
\epsilon(k) = (\pi/2)\sin k\)\n. Above this lower boundary of excitations, there is a two-parameter continuum of spin wave excitations with an upper boundary given by \(\epsilon(k) = \pi\sin(k/2)\). There are other excitations above this upper boundary.

The specific heat of the model was first calculated numerically by Bonner and Fisher \[19\]. They found that \(C\) grows linearly with \(H\) and \(\chi\) is finite at zero temperature, which shows that gapless spin excitations with a finite low energy density of states exist in this regime. When \(H = H_{c2}\), both \(\chi\) and \(C/T\) vary as \(1/\sqrt{T}\) at low temperature; the extrapolated value of \(\sqrt{T\chi}\) and \(C/\sqrt{T}\) at zero temperature are 0.152 and 0.22, respectively. The divergency of \(\chi\) and \(C/T\) at \(T = 0\) implies that the density of states of spin excitations is divergent at zero energy when \(H = H_{c2}\). Above \(H_{c2}\), there is a gap in the excitation spectrum as both \(\chi\) and \(C/T\) drop to zero exponentially at low temperatures. The value of the gap estimated from the low temperature behavior of \(\chi\) and \(C\) grows linearly with \(H - H_{c2}\).

Figure 2 shows the TMRG results for a number of thermodynamic quantities of the S=1/2 antiferromagnetic Heisenberg model in various magnetic fields with \(m = 81\) and \(\tau = 0.1\). At zero field, the TMRG reproduces accurately the results which were previously obtained by the Bethe ansatz or conformal field theory. The extrapolated zero field zero temperature values of the internal energy \(U(T)\) (i.e. ground state energy), the spin susceptibility \(\chi(T)\) and the linear coefficient of the specific heat \(C(T)\), are -0.443, 0.109 and 0.66, respectively. In all the fields which we studied, the peak position of \(\chi(T)\) is located at a temperature which is about twice of the peak temperature of \(C(T)/T\). This is due to the fact that \(\chi(T)\) is a measure of two-particle excitations and \(C(T)/T\) is only a measure of one-particle density of states. The maximum of \(\chi\) when \(H = 0\) is approximately equal to 0.147 at \(T = 0.64\), consistent with the Bethe ansatz calculation \[22\].

There is a significant change in the temperature dependences of \(\chi\) and \(C\) when \(H\) is below and above a critical field \(H_{c2} = 2\). Below \(H_{c2}\), both \(C/T\) and \(\chi\) are finite at zero temperature, which shows that gapless spin excitations with a finite low energy density of states exist in this regime. When \(H = H_{c2}\), both \(\chi\) and \(C/T\) vary as \(1/\sqrt{T}\) at low temperature; the extrapolated value of \(\sqrt{T\chi}\) and \(C/\sqrt{T}\) at zero temperature are 0.152 and 0.22, respectively. The divergency of \(\chi\) and \(C/T\) at \(T = 0\) implies that the density of states of spin excitations is divergent at zero energy when \(H = H_{c2}\). Above \(H_{c2}\), there is a gap in the excitation spectrum as both \(\chi\) and \(C/T\) drop to zero exponentially at low temperatures. The value of the gap estimated from the low temperature behavior of \(\chi\) and \(C\) grows linearly with \(H - H_{c2}\).

Figure 3 shows the longitudinal and transverse correlation lengths of the S=1/2 model in different applied fields. When \(H = 0\), \(\xi_x = \xi_z\) diverges at zero temperature.
and the slope of $\xi_z^{-1}$ at low temperature is approximately equal to 2, in agreement with the thermal Bethe ansatz as well as the $k=1$ WZW $\sigma$ model result.

$$\xi_z^{-1} = T \left[ 2 - \left( \frac{T_0}{T} \right)^{-1} \right] \quad (7)$$

In the presence of magnetic field, $\xi_z$ is substantially suppressed and becomes finite at zero temperature. As the correlation length is inversely proportional to the energy gap of excitations, the finiteness of $\xi_z$ at $T = 0$ means that the longitudinal spin excitation modes are massive in a field. There is a small dip in the curve of $\xi_x$ at $T \sim 0.4$ when $H = 0.2$ or at $T \sim 0.6$ when $H = 1$. This dip feature of $\xi_z$, as will be shown later, appears also in large $S$ systems.

The effect of the applied field on the transverse spin excitation modes is weaker than the longitudinal modes. The transverse spin excitations become massive only when $H > H_{c2}$. Below $H_{c2}$, $\xi_x$ drops to zero linearly with $T$, as for the case $H = 0$. When $H = H_{c2}$, $\xi_x$ drops to zero as $\sqrt{T}$. Clearly the thermodynamics of the Heisenberg model in a field is mainly determined by the transverse excitation modes at low temperatures.

A simple understanding of the above results can be obtained from an equivalent spinless fermion model of the $S=1/2$ Heisenberg model:

$$\hat{H} = \sum_{i} \left[ -\frac{1}{2} c_{i+1}^\dagger c_i + c_i^\dagger c_{i+1} + (H - 1) c_i^\dagger c_i + \left( \frac{1}{4} - H \right) + c_i^\dagger c_i c_{i+1}^\dagger c_{i+1} \right], \quad (8)$$

where $c_i$ a spinless fermion operator which is linked to the $S = 1/2$ spin operator by the Jordan-Wigner transformation $c_i = S_i^y \exp(i \sum_{l<i} c_l^\dagger c_l)$. The magnetic field is equivalent to a chemical potential for the fermions. When $H=0$, the ground state has zero uniform magnetization, corresponding to a half filled fermion band. As $H$ increases, the ground state is ferromagnetically polarized and the Fermi energy shifts down. When $H$ is smaller than the critical field $H_{c2}$, the ground state of this fermion model has no gap but the spin orientation is canted, i.e. in an incommensurate state. The pitch angle of this incommensurate ground state, namely the wave vector at which the maximum of the spin-spin correlation function appears, can be estimated from the Fermi momentum of non-interacting fermions as $2k_F = \left[ 1 - 2M_z(H) \right] \pi$. This value of $k_F$ is not normalized by interactions according to the Luttinger theorem.

Above $H_{c2}$, there are no fermions at the ground state. At low temperature, the number of fermions excited from the ground state are rare. Thus, as a good approximation, the interaction term in (8) can be ignored at low temperatures. For the non-interacting system, the energy dispersion of fermion excitations from the ground state is given by $\varepsilon_k = H - (1 + \cos k)$, which has a gap of $H - H_{c2}$. When $H = H_{c2}$, $\varepsilon_k = (1 - \cos k)$, the density of states of excited fermions varies as $1/\sqrt{\varepsilon}$ at low energy. From the standard theory of noninteracting fermions, it is straightforward to show that this singular density of states will cause both $\chi$ and $C/T$ to diverge as $1/\sqrt{T}$ at low temperature. When $H > H_{c2}$, there is a gap in the fermion excitations, both $\chi$ and $C$ should decrease exponentially at low temperature. These results are just what we found in Figure 2.

**FIG. 3.** (a) $1/\xi_x$ and (b) $\xi_x$ vs $T$ for the spin-1/2 Heisenberg models. $\tau = 0.1$ and $m = 81$ are used in the TMRG calculations. The circles and squares are thermal Bethe ansatz results.

**B. $S=1$**

As mentioned previously, there are two critical fields in the spin-1 Heisenberg model, $H_{c1}$ and $H_{c2}$: below $H_{c1}$, the ground state is a massive spin singlet; above $H_{c2}$, the ground state becomes a fully polarized ferromagnetic state; between $H_{c1}$ and $H_{c2}$, the ground state is massless and has a finite magnetization. The temperature dependence of thermodynamic quantities of the S=1 model below, above and (approximately) at these critical fields is shown in Fig. 4.

At zero field both $\chi(T)$ and $C(T)$ drop exponentially with decreasing $T$ at low temperatures due to the opening of the Haldane gap. In this case the ground state
energy extrapolated from the internal energy $U(T)$ is -1.4015, in agreement with the zero-temperature DMRG result \[25\]. The ground state excitation gap $\Delta$ can be determined from the temperature dependence of $\chi$ and $C$ at low temperatures. If we adapt the ansatz that the low-lying excitation spectrum has approximately the form \[26\],

$$
\varepsilon(k) = \Delta + \frac{v^2}{2\Delta} (k - \pi)^2 + O((k - \pi)^3), \quad (9)
$$

where $v$ is the spin wave velocity, it is then straightforward to show that, when $T \ll \Delta$, the spin susceptibility and the specific heat are

$$
\chi(T) \approx \frac{1}{v} \sqrt{\frac{2\Delta}{\pi T}} e^{-\Delta/T}, \quad (10)
$$

$$
C(T) \approx \frac{3\Delta}{v\sqrt{2\pi}} \left( \frac{\Delta}{T} \right)^{3/2} e^{-\Delta/T}, \quad (11)
$$

irrespective of the statistics of the excitations. Taking the ratio between $\chi(T)$ and $C(T)$ gives

$$
\Delta = \lim_{T \to 0} \frac{2TC(T)}{3\chi(T)}. \quad (12)
$$

This is a very useful equation for determining $\Delta$, especially from the point of view of experiments, since both $\chi(T)$ and $C(T)$ are experimentally measurable quantities.

Fig. 5 shows $\sqrt{2TC(T)/3\chi(T)}$ as a function of $T$ for the S=1 Heisenberg model at zero field. By extrapolation, we find that $\Delta \sim 0.41$ in agreement with the zero temperature DMRG \[25\] and exact diagonalization \[28\] results. Given $\Delta$, the value of $v$ can be found from Eq. \[10\] in the limit $T \to 0$. The value of $v$ we found is $\sim 2.45$, consistent with other numerical calculations \[26\].

![FIG. 5](image_url)

FIG. 5. $(2TC(T)/3\chi(T))^{1/2}$ vs $T$ for the S=1 Heisenberg model. ($m = 100$ and $\tau = 0.1$)

At the two critical fields, $H_{c1} \sim 0.4105$ and $H_{c2} = 4$, both $\chi(T)$ and $C(T)/T$ diverge as $T^{-1/2}$ at low temperatures. This divergence, as for the $S=1/2$ case, is due to the square-root divergence of the density of states of the low-lying excitations. At $H_{c1}$, one branch of the $S=1$ excitations becomes massless and the low-energy excitation spectrum is approximately given by

$$
\varepsilon(k) \sim \frac{v^2}{2\Delta} (k - \pi)^2. \quad (13)
$$

If we assume that these excitations are fermion-like, i.e. satisfy the Fermi statistics (a short-range interacting Bose system is equivalent to a system of free fermions), then it is simply to show that when $T \ll \Delta$

$$
\chi(T) \approx \frac{1}{3\pi v} \sqrt{\frac{2\Delta}{T}}, \quad (14)
$$

$$
C(T) \approx \frac{1}{2\pi v} \sqrt{2\Delta T}. \quad (15)
$$

Thus in the limit $T \to 0$,

$$
T^{1/2}\chi(T) = \frac{\sqrt{2\Delta}}{3\pi v} \sim 0.4, \quad (16)
$$

$$
T^{-1/2}C(T) = \frac{\sqrt{2\Delta}}{2\pi v} \sim 0.6. \quad (17)
$$

By extrapolation, the TMRG result gives $T^{1/2}\chi|_{T \to 0} \sim 0.45$, which is close to that given by Eq. \[14\] - the value

![FIG. 4](image_url)

FIG. 4. Thermodynamic quantities for the spin-1 Heisenberg model in five applied fields, $H = 0$ (or 0.05), 0.4105, 2, 4, and 4.5. When $H = 0$ and 0.4105, $F(T)$ and $U(T)$ are almost indistinguishable in the figure. When $H = 0.4105$ or 4, $F(T)$ and $U(T)$ are almost indistinguishable in the figure. When $H = 0.4105$ or 4, $T^{1/2}\chi(T)$ and $2C(T)/T^{1/2}$ (dotted lines) are shown in (d) and (f), respectively. $\tau = 0.1$ and $m = 100$ are used in the TMRG calculations.
of \( T^{-1/2}C(T) \) is difficult to determine accurately from the TMRG result since the error of \( C(T) \) at low temperature is larger than \( C(T) \) itself.

When \( H > H_{c1} \), \( \xi^{-1}_x \) drops rather sharply at some temperatures. These sharp drops of \( \xi^{-1}_x \) happen when the second and third eigenvalues of the transfer matrix with \( \sum_k \sigma^k = 0 \) cross each other. The physical consequence of these sudden changes in the longitudinal correlation length is still unknown.

### C. S=3/2

The thermodynamic behaviors of the S=3/2 Heisenberg model, as shown in Fig. 5, are similar to those of the S=1/2 model. When \( H < H_{c2} = 6 \), \( \chi \) is always finite at zero temperature, indicating that the ground state is massless; above \( H_{c2} \), the ground state is fully ferromagnetic polarized and a gap is open in the excitation spectrum; at \( H_{c2} \), both \( \chi(T) \) and \( C(T)/T \) diverge as \( T^{-1/2} \). At zero field, the susceptibility data, extrapolated to zero temperature, gives \( \chi(0) \sim 0.67 \), consistent with recent numerical calculations [29].

The crossover from quantum to classical behavior can be clearly seen (Fig. 6) by comparing the zero field susceptibility and specific heat of the S=1/2, 1 and 3/2 spin chains with the corresponding results of the classical Heisenberg spin chain: [31]

\[
\chi(T) = \frac{1}{3T} \frac{1 - u(T)}{1 + u(T)}, \quad u(T) = \coth \frac{1}{T} - T, \quad (18)
\]
\[ C(T) = 1 - \frac{1}{T^2 \sinh^2 (1/T)}. \]  

(19)

At high temperatures, \( T/S(S + 1) > 1 \), the quantum results approach asymptotically to the classical ones. The agreement between the quantum and classical results persist down to progressively lower temperatures as \( S \) increases. At low temperatures, however, the difference between the results of the \( S=3/2 \) system and those of the classical model is still very large, indicating the importance of the quantum effects in the study of quantum spin chains. (Note for the classical Heisenberg model, \( C(T) \) does not vanish at zero temperature. This is a unrealistic feature of this model.)

D. Zero temperature magnetization

Figure 9 shows \( M_z(T=0) \), extrapolated from the finite temperature TMRG data of \( M_z(T) \), for the \( S=1/2, 1, \) and \( 3/2 \) systems. For comparison the Bethe ansatz result \[ C(T) = 1 - \frac{1}{T^2 \sinh^2 (1/T)}. \]  

(19) for the \( S=1/2 \) Heisenberg model is also shown in the figure. With increasing \( S \), we found that \( M_z \) tends to approach to its classical limit \( (S \to \infty) \) where \( M_z \) increases linearly with \( H \), i.e. \( M_z/S = H/H_{c2} \).

![Graph showing the zero field specific heat and susceptibility vs \( T/S^2 \) for the \( S=1/2, 1, \) and \( 3/2 \) spin chains.](image1)

![Graph showing the normalized zero temperature magnetization \( M_z/M_c \) as a function of \( H/H_c \).](image2)

For the \( S=1/2 \) system, the TMRG result agrees well with the Bethe ansatz one. A least square fit to the curve of \( M_z \), up to the fourth order term of \( \sqrt{H_{c2} - H} \), gives \( M = M_c - a_1 \sqrt{H_{c2} - H} + a_2 (H_{c2} - H) - a_3 (H_{c2} - H)^{3/2} + a_4 (H_{c2} - H)^2 \), with \( a_1 \approx 0.448, a_2 \approx 0.123, a_3 = 0.05 \) and \( a_4 = 0.00744 \). \( a_1 \) agrees very accurately with the exact value \( \sqrt{2}/\pi \). In the weak field limit, the asymptotic behavior of \( M_z \) is

\[ M_z \approx \frac{H}{\pi^2} \left(1 - \frac{1}{2 \ln(H/H_{c2})}\right), \]

(20)
as predicted by the Bethe Ansatz theory \[ C(T) = 1 - \frac{1}{T^2 \sinh^2 (1/T)}. \]  

(19)

For the \( S=1 \) model, \( M_z(T=0) \) becomes finite when \( H > H_{c1} \). In a very narrow regime of field near \( H_{c1} \), \( M_z(0) \) varies approximately as \( \sqrt{H - H_{c1}} \), in agreement with the prediction of the Bose condensation theory. But the difference between the result of the Bose condensation theory

\[ M_z(T=0) \approx \frac{\sqrt{2(H - H_{c1})}}{\pi \Delta} \]  

(21)

and that of the TMRG becomes already significant when \( H - H_{c1} = 0.04 \).

Near \( H_{c2} \), \( M_z \) approaches to its saturation value \( M_c = S \) as a function of \( \sqrt{H_{c2} - H} \) for the three spin systems we study. For the \( S=1/2 \) and \( 1 \) systems, the TMRG
results agree very accurately with the Bethe ansatz result \[ M_z = 1 - \frac{2}{\pi S} \sqrt{1 - \frac{H}{H_{c2}}} \] (22)

For the S=3/2 system, the asymptotic regime of \( H \) is very narrow, we cannot do a detailed comparison between the TMRG result and Eq. (22). The magnetization curve does not show a plateau at \( M_z = 1/2 \), in agreement with other studies [3].

E. Staggered susceptibility

To calculate the staggered susceptibility, we add a staggered magnetic field \( H_s \) to the Hamiltonian \( \hat{H} \). The staggered magnetization is then calculated in a way similarly to the calculation of the uniform magnetization. The staggered susceptibility \( \chi_s \) is obtained by differentiating the staggered magnetization with respect to \( H_s \). For half-odd-integer spin chains \( \chi_s \) diverges as \( T^{-1} \) at low temperatures. Thus the staggered magnetization becomes saturated at low temperatures when \( \chi_s(T)H_s > S \), since the maximum value of the staggered magnetization per spin is \( S \). This means that to estimate accurately the zero field staggered susceptibility the staggered field used should satisfy the condition \( H_s \ll S/\chi_s(T_{min}) \), where \( T_{min} \) is the lowest temperature to study.

\[ \chi_s(T) = \frac{\partial M_z}{\partial H_s} \]

FIG. 10. The staggered susceptibility \( \chi_s(T) \) at zero field. The parameters used for the S=1/2, 1, and 3/2 chains are \( (H_s, \tau, m) = (0.0001, 0.1, 140), (0.0001, 0.05, 100), \) and \( (0.0001, 0.025, 81) \), respectively.

Fig. 10 shows the temperature dependence of \( \chi_s \) for the S=1/2, 1, and 3/2 spin chains. At low temperatures, \( \chi_s \) for the S=1/2 model is expected to have the following asymptotic form

\[ \chi_s = \frac{D_s}{T} \sqrt{\frac{T}{T \chi}} \] (23)

IV. CONCLUSION

In conclusion, the temperature dependence of the susceptibility, specific heat, and several other quantities of the quantum Heisenberg spin chains with spin ranging from 1/2 to 3/2 in a finite or zero applied magnetic field are studied using the TMRG method. At high temperatures, the quantum results for the specific heat as well as other thermodynamic quantities approach asymptotically to the classical ones for both the integer and half-integer spin systems. At low temperatures, however, the quantum effect is strong and the integer spin chains behave very differently than the half-integer spin chains. For the S=1 model, both \( \chi \) and \( C/T \) decay exponentially at low temperatures due to the opening the Haldane gap. For the S=1/2 and 3/2 spin chains, there is no gap in the excitation spectrum and both \( \chi \) and \( C/T \) are finite at zero temperature. The thermodynamics of the Heisenberg spin chains in an applied field is mainly determined by the transverse excitation modes. At low temperatures, \( \chi \), \( C/T \), and the transverse correlation length \( \xi \), diverge as \( T^{-1/2} \) at \( H_{c2} \) for the S=1/2 and 3/2 models and at both \( H_{c1} \) and \( H_{c2} \) for the S=1 model. This square-root divergence indicates that the low energy spin excitations have a square-root divergent density of states at these critical fields. Our data agree well with the Bethe ansatz, quantum Monte Carlo, and other analytic or numerical results.

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