Low-Temperature Properties of the Randomly Depleted Heisenberg Ladder

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Low-temperature thermodynamic properties of the spin-$1/2$ Heisenberg ladder system with non-magnetic impurities are discussed using an effective Hamiltonian for the impurity-induced spins in the background of a spin liquid with a gap. It is shown that the uniform susceptibility shows Curie-like behavior in high-, intermediate-, and low-temperature regimes, with three different Curie constants. The ratio of specific heat to temperature, $C/T$, is divergent in the low-temperature limit, reflecting a singular distribution of the effective couplings among the impurity spins.

KEYWORDS: quasi-one-dimensional spin system, random spin chain

Quasi-one-dimensional quantum spin liquids with a spin excitation gap have attracted much interest for more than a decade. One recent example of interest is the spin-$1/2$ ladder system because of its relationship to cuprate superconductors. These spin ladders can be modeled by a nearest-neighbor Heisenberg Hamiltonian of the form

$$H = J \sum_{i} \sum_{\mu=1,2} S_{i,\mu} \cdot S_{i+1,\mu} + J \sum_{i} S_{i,1} \cdot S_{i,2}$$

for the case of a two-leg ladder, where $S_{i,\mu}$ denotes the spin operator on rung $i$ and leg $\mu$ (see Fig. 1(a)). Considerable effort has been invested both experimentally and theoretically to study the properties of these systems. We may say that by now, regular ladders, in particular, those with two legs, are well understood both qualitatively and quantitatively. In general ladder systems with an even number of legs have a resonating valence bond (RVB) ground state with a spin gap, while an odd number of legs leads to gapless excitations in a ground state with quasi-long-range order. The spin gap is largest for the system with two legs, where numerical data show $\Delta \approx 0.5J$. Therefore, in real two-leg ladder systems, $\Delta$ can be very large, as the examples $(\text{VO})_2 \text{P}_2 \text{O}_7$ with $\Delta \sim 40K$ and $\text{SrCu}_2 \text{O}_3$ with $\sim 400K$ show.

An interesting new aspect arises, if we take disorder into account. The type of disorder we are interested in here, is the depletion of spins. This may occur when ions delivering the spin degrees of freedom are replaced at random by other ions without spins, by accident or by intentional doping [Fig. 1(b)]. For example, in $\text{SrCu}_2 \text{O}_3$ some $\text{Cu}$-ions can be substituted by nonmagnetic $\text{Zn}$-ions. It has been observed experimentally that in systems with a dimer ground state, such a depletion introduces a strong component of staggered moments. This effect has recently been investigated theoretically.

In the vicinity of a nonmagnetic impurity the spins develop a strong staggered correlation, generating an effective spin doublet. These effective spins dominate the low-temperature physics, since, due to the presence of the spin gap, all other spin degrees of freedom disappear at small enough energy scales. For a low, but finite concentration of impurities, the correlation among these effective spins will play an important role in the low-energy properties. It is the aim of this letter to show some consequences of this correlation which may be tested experimentally.

![Fig. 1. (a) Regular spin ladder system, (b) depleted spin ladder system.](image-url)

Obviously each empty site (nonmagnetic impurity) in the RVB ground state of a two-leg spin ladder represents a spin $S = 1/2$. In the following we will assume that the impurity concentration is sufficiently low such that the idea of a spin-$1/2$ degree of freedom associated separately with each impurity is valid. The coupling between these impurity spins is very weak and short-ranged, because it is mediated by the spins which participate in the formation of the RVB spin liquid state. Before addressing the issue of coupling strengths we discuss a more qualitative aspect. It is intuitively clear that the coupling between the effective spins can be either ferromagnetic or antiferromagnetic, depending on their relative locations. We can show this on a rigorous basis by considering a ladder system with two impurities at sites $(i_1, \mu_1)$ and $(i_2, \mu_2)$.
(i_2, \mu_2). The nature of the effective coupling can be determined by finding the total spin quantum number of the ground state. This can be straightforwardly done using Marshall’s theorem [3] which states that the spin quantum number of the ground state of \( \mathcal{H} \) in eq. (1) is identical to that of the Hamiltonian,

\[
\mathcal{H} = \sum_{i \in A} \sum_{j \in B} S_i \cdot S_j, \tag{2}
\]

where \( A \) and \( B \) denote the sets of sites belonging to the two different sublattices (note that the ladder system is a bipartite lattice). The eigenenergies \( \tilde{E} \) of \( \mathcal{H} \) depend on three parameters: \( S_{\text{tot}} \) (\( S_{\text{tot}} = \sum S_i \)), \( S_A (S_A = \sum_{i \in A} S_i) \) and \( S_B (S_B = \sum_{i \in B} S_i) \). They are simply given by

\[
\tilde{E}(S_{\text{tot}}, S_A, S_B) = \frac{1}{2} [S_{\text{tot}} (S_{\text{tot}} + 1) - S_A (S_A + 1) - S_B (S_B + 1)]. \tag{3}
\]

The ground state corresponds to the case when \( S_A \) and \( S_B \) have their maximal and \( S_{\text{tot}} \) its minimal value (\( = |S_A - S_B| \)). This immediately leads to the well-known result that if the number of sites on the two sublattices is identical, then \( S_A = S_B \) and the ground state is a total spin singlet.

We can now apply this theorem to our problem. If the two impurities are on different sublattices, they remove one site from each sublattice. Thus the ground state again has \( S_A = S_B \) and is a singlet, implying that the coupling between the two impurity spins is antiferromagnetic. On the other hand, if the two impurity sites lie on the same sublattice, then the spin quantum number of this sublattice is smaller by 1 than that of the other and \( S_{\text{tot}} = 1 \), a triplet ground state. This corresponds to a ferromagnetic coupling. Consequently, the low-energy properties of the randomly depleted spin ladder may be described effectively by a model of spins \((S = \frac{1}{2})\) with couplings of random strength and random sign. The low-temperature properties of this type of system have recently been investigated by means of a real-space renormalization group scheme [4] based on earlier studies by Ma and co-workers [11,12]. In the following we discuss how these results can be applied to this system.

Let us first consider the uniform susceptibility of this system. At high temperatures \((k_B T > J)\) the spins are essentially free and the susceptibility per site obeys the Curie law,

\[
\chi(T) = \frac{\mu_B^2}{4k_B T}, \tag{4}
\]

where \( \mu_B \) is the Bohr magneton and \( k_B \) is the Boltzmann constant. It is clear that for temperatures below the spin gap, only the effective impurity spins contribute to the susceptibility, because the other spins have frozen out. This shows up as a sharp drop in the susceptibility for \( T < \Delta \). Since the impurity spins are only weakly coupled, they will yield a Curie-like susceptibility in an intermediate temperature regime:

\[
\chi(T) = \frac{\mu_B^2 z}{4k_B T}, \tag{5}
\]

where \( z \) is the impurity density \((z \ll 1)\). At lower temperatures, these impurity spins start to correlate due to their interaction. First the two spins with the strongest mutual coupling freeze into either a singlet or a triplet state, depending on the sign of the interaction. In the case of the triplet configuration, they act as a single new spin \((S = 1)\) coupled via weaker effective interactions to its two adjacent impurity spins. For the singlet case, however, these spins no longer contribute as degrees of freedom, but still mediate an effective interaction between the two adjacent impurity spins through virtual excitations. In this way we find the equivalent effective spin system where the strongest bond of the original system was integrated out. With decreasing temperature, the next strongest pair forms a single spin with new effective coupling to its neighbors and so on. By iteration of this process an effective spin system gradually evolves, in which spin degrees of freedom consist of large clusters of randomly correlated impurity spins. The formation of these effective spins is determined by the energy scale \( k_B T \); all degrees of freedom with correlation energies larger than this energy scale are frozen into such effective spins. Consequently these effective spins behave essentially independently, since the correlation energies among them are smaller than the thermal energy. Using this picture we can calculate the uniform susceptibility in the following way.

Let us assume that the average size of the cluster of correlated spins contains \( n \) rungs. Note that \( n \) is a monotonic function of the temperature. Now we can estimate the average size of the effective spin associated with the cluster by again applying Marshall’s theorem. Consider a Heisenberg ladder containing \( n \) rungs where \( 2zn \) spins are randomly depleted on average. The effective spin size of the cluster corresponds to the ground-state spin quantum number \( S_{\text{tot}} \) of this finite-length Heisenberg ladder, which is, on average,

\[
\langle S_{\text{tot}} \rangle = \langle |S_A - S_B| \rangle = \frac{1}{2} \langle |N_A - N_B| \rangle, \tag{6}
\]

where \( N_A (N_B) \) is the number of depleted sites on the \( A (B) \) sublattice and the average is taken over the impurity configuration. This can be easily estimated from a random-walk picture:

\[
\langle S_{\text{tot}} \rangle = \sqrt{n z \frac{1}{2}} \tag{7}
\]

for \( nz \gg 1 \). Thus the uniform susceptibility per site becomes

\[
\chi(T) = \frac{\mu_B^2}{3k_B} \langle S_{\text{tot}}^2 \rangle \frac{1}{2n(T)} = \frac{\mu_B^2 z}{12k_B T}. \tag{8}
\]

This result means that the susceptibility also follows a Curie law at sufficiently low temperatures. However, the Curie constant for \( T \to 0 \) is different from that in eq. (4). Consequently, we expect to see crossovers in the Curie constant, as schematically shown in Fig. 2. Our prediction is that the Curie constant drops by a factor of \( 1/3 \) from the intermediate- to the low-temperature regime.

The characteristic temperature \( T^* \) where this
crossover occurs is set by the average coupling strength among the impurity spins (Fig. 2). Here we attempt to give a rough estimate of this energy scale based on a simplified model of the spin gap state. Suppose only two spins, at sites (0, 0) and (j, µ), are depleted in the Heisenberg ladder, and the resulting impurity spins interact with each other by exchanging a spin triplet excitation in the RVB spin liquid. For calculating the long-distance behavior of this interaction, it is sufficient to consider an approximate dispersion of these excitations. We adopt the dispersion given by Troyer et al., which they used to fit numerical data of the regular two-leg spin ladder system. Their momentum dependence for the spin triplet excitation energy has the form

$$E_k = \sqrt{\Delta^2 + v^2 (k - \pi)^2},$$

where k is the momentum along the leg. Note that this excitation corresponds to an odd-parity state along the rung. The effective interaction can be obtained, in a similar way to the RKKY treatment, by second-order perturbation:

$$\tilde{J}(j, \mu) \approx \frac{a J^2}{v} (-1)^{j+\mu} \int_{-\pi}^{\pi} \frac{dk}{\sqrt{(\Delta/v)^2 + k^2}} e^{i k j} \approx \frac{2a J^2}{v} (-1)^{j+\mu} K_0(j/\ell_0),$$

where a is an unknown constant of order unity coming from the matrix elements. The parameters used by Troyer et al. are $\Delta \approx 0.5 J$ and $v = 1.8 J$. Thus we obtain

$$\tilde{J}(j, \mu) \approx 1.1 a J (-1)^{j+\mu} K_0(j/\ell_0).$$

It is important that the length scale appearing in the modified Bessel function $K_0, \ell_0 = v/\Delta \approx 3.6$, is rather short, and equivalent to the spin-spin correlation length in the regular ladder. Therefore it seems reasonable to assume that the effective spin system for low-temperature physics ($T < \Delta$) is described well by considering only nearest-neighbor Heisenberg coupling.

For a given $z$ the distribution of distance between neighboring impurities is $P(\ell) = 2z \exp(-2z\ell)$, which gives an average distance $\langle \ell \rangle$ of $1/2z$. This leads to an average coupling strength of

$$\langle \tilde{J} \rangle \approx 1.1 a J \sqrt{\pi z \ell_0 e^{-1/2z\ell_0}}.$$  \hspace{1cm} (12)

Thus, for $5\%$ of depleted sites we get $\langle \tilde{J} \rangle \approx 5 \cdot 10^{-2} a \Delta$, which could be on the order of $10 K$ for $\Delta \approx 400 K$, as in SrCu$_2$O$_3$.

So far we have ignored the fact that ladder systems can be easily disconnected if we remove sites randomly. Therefore the above analysis is valid only when a short-range correlation among the impurity positions is present, which prohibits configurations leading to decoupled segments of the ladder. If we ignore this type of correlation, then the ladder decays into decoupled segments of finite length, which, on average, contain $1/z^2$ rungs and $2/z$ impurities. This average length $1/z^2$ serves as a low-energy cutoff. This means that the process of developing spin correlation with decreasing energy scale is interrupted once all spins in a segment are frozen into its ground-state configuration. Hence in the low-temperature limit, each segment behaves as an independent effective spin degree of freedom, yielding a Curie-like temperature dependence of the susceptibility.

The Curie constant is naturally expected to be somewhere between the values given in eqs. (8) and (9). We can estimate this Curie constant by calculating the mean value of the ground-state spin quantum number $S'$ of the segments. For a given number n of impurity spins in a segment, we obtain

$$S'(n) = \left \langle \left ( \sum_{i=1}^{n} S_i^z \right )^2 \right \rangle^{1/2}$$

$$= \left [ \frac{1}{2^n} \sum_{m=0}^{n} \frac{n!}{m!(n-m)!} \left ( \frac{n-2m}{2} \right )^2 \right ]^{1/2}$$

$$= \sqrt{n},$$

(13)

where $S_i^z$ denotes impurity spins $\pm 1/2$. Noting that the distribution of n is given by $\tilde{P}(n) \approx (z/2) e^{-nz/2}$, we obtain the Curie constant

$$\mu_B^2 \left \langle S'(n)|S'(n)+1\right \rangle \approx \frac{\mu_B^2}{12k_B^2} \left ( z + \sqrt{\frac{z}{2}} \right )^{3/2},$$

(14)

which gives only a small deviation from eq. (8) for $z \ll 1$.

Next we discuss the low-temperature behavior of the specific heat. For this purpose we need to know the distribution of the effective couplings $\tilde{J}$. The fact that the coupling strength decays exponentially with the distance leads to a distribution which is rather singular for $J \rightarrow 0$. In this limit, it is approximated by

$$D(|\tilde{J}|) \approx \int d\ell \, \tilde{P}(\ell) \delta(|\tilde{J}| - J_0 \sqrt{\ell_0/\ell} e^{-\ell/\ell_0})$$

$$\approx \frac{2z \ell_0}{J_0} \left ( \frac{|\tilde{J}|}{J_0} \right )^{2z \ell_0 - 1},$$

(15)

where we have neglected small logarithmic corrections. The smaller the concentration $z$, the more of a singular distribution we obtain. It was shown by Westerberg and co-workers [13] that in a real-space renormalization group treatment, the distribution of couplings approaches a universal singular form [4] for $J \rightarrow 0$. This leads to

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{Curie_constant}
\caption{Schematic picture of the three regimes of the Curie constant, $\chi T$. The first crossover temperature is the spin gap $\Delta$ and the second, $T^*$, is related to the average coupling strength.}
\end{figure}
a universal low-temperature behavior of various quantities such as the specific heat; at very low temperatures, the specific heat $C$ would follow a power law, and the ratio $\frac{C(T)}{T}$ would be more singular than that of a ferromagnet ($\frac{C_{\text{ferro}}}{T} \propto T^{-1/2}$ for $T \to 0$). This can be easily seen from the following argument.

As we have already discussed, at low temperatures many impurity spins correlate in clusters which then behave more or less as single spin degrees of freedom. The number of correlated impurity spins, $n(\gg 1)$, at temperature $T$ can be estimated by noting that the finite-size gap, $\Delta_n$, to the first excited state in this $n$ spin system should be on the order of $k_B T$. It is natural to assume that $\Delta_n \propto n^{-1/\alpha}$, where the exponent $\alpha$ should be determined from $\Delta(\{J\})$. From eq. (7) we get $S'(n) \propto \Delta_{\alpha}^{-\alpha/2} \propto T^{-\alpha/2}$. We can then estimate the entropy $\sigma$ per site by assuming that each effective spin is essentially independent: $\sigma = z \ln[2S'(n)+1]/n$. From these relations, we get $\sigma(T) \propto z T^{\alpha} \ln(1/T)$, yielding $C(T) \propto z T^{\alpha} \ln(1/T)$ to leading order in $T$. If the couplings $J$ between the impurity spins were all uniform and ferromagnetic, $C(T) \propto T^{1/2}$. With random distribution of coupling, we expect that the low-lying excitations are, in general, softer, because they are dominated by spin fluctuations around the weakest couplings. This leads to the conclusion that $\alpha \leq 1/2$, in agreement with ref. [3]. Hence, $C(T)/T \propto T^{-1/2}$ for $T \to 0$.

From these arguments we can expect the following temperature dependence of the specific heat. At high temperatures the specific heat behaves essentially like that of the regular Heisenberg ladder. It has a peak at $k_B T \sim J$ and drops towards lower temperature due to the presence of the spin gap. Note that the staggered spin environment of each impurity introduces a discrete spectrum of localized excitations in the uniform spin gap, which can smear the gap behavior. As the temperature is decreased further, it shows a broad peak or shoulderlike structure around $k_B T \approx \langle |J| \rangle$ due to the interaction between the impurity spins, and it becomes the anomalously powerful law behavior discussed above for $T \to 0$. However, in the case of uncorrelated impurity positions, this power law behavior will be cut off by the finite-size gap determined by the average length $1/z^2$ and the coupling distribution $D(J)$. Obviously the ground state of the whole system will have a large degeneracy, unless there is residual interaction between “decoupled” segments.

In summary, we have found that at low temperatures the randomly depleted spin ladder system behaves in many respects like a random spin system with ferro- and antiferromagnetic couplings. Nevertheless, we emphasize that the impurities induce a staggered correlation which is, although inhomogeneous, coherent on a long length scale at low temperature. This would be the dominant spin correlation feature in neutron scattering measurements. An important result of our study is that in this system correlation effects lead to three distinct temperature regimes. Of particular interest is the low-temperature regime, where Curie behavior of the uniform susceptibility appears with a nontrivial Curie constant. Furthermore, the specific heat shows an anomalous temperature dependence for $T \to 0$, as long as decoupling into segments is not significant. These properties are not restricted to two-leg ladders, but would also appear in any even-leg ladder and other systems with an RVB ground state. We believe that for a certain range of impurity doping in ladder systems, these effects would be in an experimentally accessible temperature range, in particular, for two-leg ladders with a large spin gap. In actual Heisenberg ladder systems such as SrCu$_2$O$_3$, there is certainly coupling between different ladders. Although very weak, this coupling can also introduce a low-energy cutoff for the temperature dependence of $\chi$ and $C$ and can lead to long-range order of the staggered spin correlation, as was actually observed experimentally.

This change to 3-dimensional behavior would spoil the observation of our low-temperature regime.

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