Random Exchange Heisenberg Chain for Classical and Quantum Spins

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The Heisenberg chain with random $\pm J$ bonds is studied for the quantum spin $s = 1/2$ and in the classical limit. The former is treated by high-temperature expansion and transfer matrix calculation while the latter can be analyzed exactly. The disorder leads to a $1/T$ behavior of the low-temperature susceptibility in the classical system. For $s = 1/2$ our analysis reveals a significant residual entropy at low temperature. From this we conclude that for quantum spins the susceptibility exhibits three different regimes in temperature and that the specific heat has a peak in the very low-temperature regime.

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For many decades the spin chains have attracted much attention in condensed matter physics and statistical mechanics. In recent years one-dimensional (1D) spin systems have become accessible to experimental investigation. A class of such systems is realized in materials like Sr_3CuPtO_6 which represents an antiferromagnetic chain of the Cu spins ($s = 1/2$) [1]. Another is Sr_3CuIrO_6 in which the spins of Cu and Ir, both $s = 1/2$, couple ferromagnetically. It is possible to produce alloys $SrCuPt_{1-p}Ir_pO_6$, systems of quenched bond disorder. In some alloys it was observed that the susceptibility is proportional to $1/T$ over practically the whole temperature range [2]. Motivated by these experiments, we consider here a simplified model of these systems, a spin-1/2 chain given by the Hamiltonian

$$\mathcal{H} = \sum_{i=0}^{L-1} J_i \mathbf{S}_i \cdot \mathbf{S}_{i+1} - \mu H_z \sum_{i=0}^{L-1} S_i^z , \qquad (1)$$

where all bonds J_i have the same strength, but random sign, i.e., their probability distribution is given by $P(J_i) = p\delta(J_i + J) + (1 - p)\delta(J_i - J)$ for $0 \le p \le 1$ and $J > 0$. The limit $p = 0$ corresponds to the uniform antiferromagnetic (AF) and $p = 1$ to the uniform ferromagnetic (FM) Heisenberg chain. The magnetic field H_z is uniform.

In recent theoretical studies of random spin chains mainly systems with weak disorder have been discussed [3]. Obviously, the quenched disorder is *not weak* in our case, since J gives the only energy scale in the problem. Therefore, methods applied to models with weak disorder may not lead to satisfactory descriptions in this case. We tackle this problem in two ways. First, we discuss the physical properties for the case of classical spins, where exact results can be obtained. Second, we focus on the quantum spin-1/2 system by means of a high-temperature expansion and transfer matrix calculations of some physical quantities.

The classical random bond spin problem can be mapped to the ferromagnetic spin chain problem by introducing "staggered" spins, $\tilde{\mathbf{S}}_i = \mathbf{S}_i \prod_{l=0}^{i-1} \mathrm{sgn}(-J_l)$. Thermodynamic quantities such as the internal energy are then independent of bond disorder as is given by Fisher's exact solution [4]. These staggered spins develop a long correlation length $\tilde{\xi}$ at low temperature. The original spin correlation function and susceptibility can be calculated exactly using an extension of Fisher's method. In particular, the two-spin correlation function $\Gamma(i - j)$ can be written as a product of functions $v(K)$ over all bonds between sites i and j ($i < j$):

$$\Gamma(i - j) = \langle S_i^z S_j^z \rangle = \frac{s^2}{3} \prod_{\ell=i}^{j-1} v(K_\ell), \qquad (2)$$

with $v(K_i) = \coth(2K_i) - 1/2K_i$ and $K_i = J_i s^2/k_B T$. It is straightforward to obtain the correlation function averaged over the bond disorder: $\bar{\Gamma}(i - j) = [\bar{v}(K)]^{|i-j|}$, where $\bar{v}(K) = \int dJ_i P(J_i) v(K_i) = (2p - 1)v(K)$. Thus the average correlation length is given by $\tilde{\xi} = -1/\ln[\bar{v}(K)]$. This leads to the susceptibility per spin ($L \to \infty$)

$$\chi(T) = \frac{\mu^2}{k_B T} \frac{1}{L} \sum_{i,j=0}^{L-1} \bar{\Gamma}(i - j) = \frac{\mu^2 s^2}{3k_B T} \frac{1 + \bar{v}(K)}{1 - \bar{v}(K)} . \qquad (3)$$

For $T \to 0$ we find

$$\chi(T) \approx \frac{\mu^2 s^2}{3k_B T} \frac{p - (2p - 1)/4K}{1 - p + (2p - 1)/4K} . \qquad (4)$$

The susceptibility approaches a constant value, $\chi(T \to 0) \to \mu^2/12J$ for $p = 0$ (AF) and diverges quadratically, $\chi(T \to 0) \to 4\mu^2 s^4 J/3k_B^2 T^2$ for $p = 1$ (FM). For all intermediate values of p we find a Curie-like singularity $\chi(T) \approx C(p)/T$ with $C(p) = \mu^2 s^2 p/3k_B(1 - p)$. Hence, there is in general a crossover between the $1/T$ dependence of the high-temperature (HT) regime with $\chi(T) = \mu^2 s^2/3k_B T$, independent of p, and a low-temperature (LT) regime with a p-dependent constant (see Fig. 1).

This effect can be easily understood by the following argument. In the HT limit all spins act independently.

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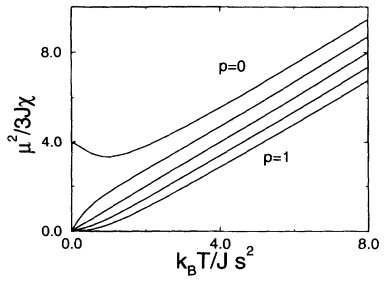

FIG. 1. Inverse susceptibility for $p = 0$, 0.25, 0.5, 0.75, and 1 for the classical spin chain.

Turning to lower temperatures the staggered spins become gradually correlated on the length scale $\tilde{\xi}(T)$ which is the correlation length of the staggered two-spin correlation function $\tilde{\Gamma}(i-j) = \langle \tilde{S}_i^z \tilde{S}_j^z \rangle = [v(K)]^{|i-j|}$, independent of p. Within the length $\tilde{\xi}(T)$ the spins act essentially as one large spin degree of freedom whose magnitude is determined by the bond disorder.

Let us consider the example of very small p, i.e., an AF chain with only few FM bonds. In the LT regime each FM bond leads to an excess spin s which contributes to a large effective spin within the length $\tilde{\xi}(T)$. Since these excess spins can be randomly up or down depending on the relative position of the FM bonds, the effective spin is $S = s[\tilde{\xi}(T)p]^{1/2}$, where $\tilde{\xi}p$ is the average number of FM bonds on a chain of length $\tilde{\xi}$. These effective spins behave independently, yielding a susceptibility per site

$$\chi(T) \sim \frac{S^2\mu^2}{3k_BT\tilde{\xi}(T)} = \frac{\mu^2 s^2 p}{3k_BT}. \tag{5}$$

The length $\tilde{\xi}(T)$ cancels so that it does not appear in the final result for $\chi(T)$. A similar argument applies for the nearly FM chain where the effective spins formed by finite FM segments of aligned spins: $\chi(T) \sim \mu^2 s^2/3k_BT(1-p)$. As a consequence of this picture we expect the magnetization to become nonlinear on a magnetic field scale H_c such that $H_c S = H_c s[\tilde{\xi}(T)p/(1-p)]^{1/2}$ is comparable to k_BT. This suggests an experimental method to measure $\tilde{\xi}(T)$ directly.

We turn now to the quantum spin model. For the treatment of this system we use high-temperature cluster expansion, where physical quantities can be easily averaged over the random $\pm J$-bond distribution for any value of p. For our 1D spin-1/2 chain we calculate a series of the internal energy $u(K)$ up to 22nd order in K and to 11th order for χ. Additionally, we performed a numerical transfer matrix calculation for $p = 1/2$ in order to compare the results of both methods. A lattice of 400 sites has been used with up to 9 Trotter slices. The disorder average has been taken over 20 samples. Details of these calculations will be published elsewhere.

First, we investigate the properties of the susceptibility for the quantum spin chain. For the uniform chain the LT behavior is well known: $\chi(T \to 0) \to \mu^2/\pi^2$ (AF) and $\chi(T \to 0) \to \mu^2 J^2/8k_B^2T^2$ (FM). Guided by the properties of the classical system we assume that bond disorder introduces a $1/T$ dependence in the LT regime. For a certain range of p the function $f(K) = T\chi(T)$ is monotonic, so that the coefficients $\mu^2 C(p)/k_B = \lim_{T\to 0} T\chi(T) = \lim_{K\to\infty} f(K)$ occur as poles in the inverted function $K(f)$. Analyzing the corresponding series by standard methods [5], we obtain the following approximate form of χ for $0 < p < 1$ and $T \to 0$:

$$\chi(T,p) \approx \frac{\mu^2}{8k_BT}\frac{p}{1-p}, \tag{6}$$

while for $T \to \infty$, $\chi(T,p) = \mu^2/4k_BT$. In Fig. 2 we plot the overall temperature dependence of the inverse susceptibility. There is a qualitative difference between the classical and the quantum systems, which is illustrated best for the case of $p = 1/2$. While the classical system does not show a crossover (Fig. 1), the quantum spin chain exhibits a clear regime change around $K \sim 1$ between the HT and LT $1/T$ behavior (see the inset of Fig. 2 for the results of the HT expansion and the transfer matrix calculation). The ratio of the coefficients for HT (C_∞) and LT (C_0) regimes is $C_\infty/C_0 \approx 2$. Hence the effective large spin introduced above to explain the behavior of the classical system is reduced so that smaller effective spins contribute to the magnetic response in the LT regime of the quantum system. For comparison we have also analyzed the spin-1 chain at $p = 1/2$, where we find that the ratio $C_\infty/C_0 \approx 3/2$ (Fig. 2, inset). This demonstrates that we approach gradually the classical limit, $C_\infty/C_0 = 1$, with increasing spin. In the following analysis, however, we will show that Eq. (6) is valid only in an intermediate temperature regime rather than in the zero-temperature limit.

In contrast to the behavior of the classical system, the thermodynamic properties are strongly affected by the presence of disorder in the quantum spin chain. Using various schemes for the analysis of series we have

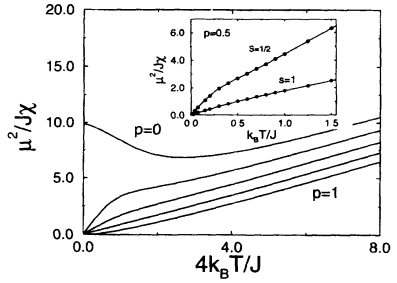

FIG. 2. Inverse susceptibility for $p = 0$, 0.25, 0.5, 0.75, and 1 for the quantum spin chain obtained by two-point Padé approximation. Inset: Inverse susceptibility of the spin-1/2 and spin-1 chain for $p = 1/2$. The solid lines are the approximations from the high-temperature expansion and the filled dots are the results obtained by transfer matrix calculation. The two methods show very good agreement.

evaluated the internal energy u assuming $u(T) - u(0) \propto T^{1+\alpha}$ [5]. It is well known that the exponent is $\alpha = 1$ for the uniform AF and $\alpha = 1/2$ for the uniform FM system. For some values of p in the range $1/2 \leq p \leq 1$ we obtain estimates of α from our series by ratio method (Table I). Using the information about α in a two-point Padé approximation [5], we plot the overall temperature dependence of the specific heat (Fig. 3). The quality of these approximations is demonstrated by the comparison with data obtained from finite size calculations by Blöte [6] for $p = 0,1$ and by our transfer matrix calculation for $p = 1/2$. The agreement is very good down to temperatures $k_BT \approx J/5$. The form of the Padé approximants suggests that the density of states behaves as $\rho(\omega) \propto \omega^{\alpha-1}$ for small ω which we believe to be valid for an intermediate-energy scale. Hence, the large values of α for $0 < p < 1$ (Table I) indicate a depletion of the density of states in this energy scale which is still accessible by our high-temperature expansion treatment. In the following we will show that this interpretation is indeed reasonable. However, we also find an enhancement of the density of states for the very low-energy scale; i.e., random exchange coupling leads to a redistribution of the density of states from the intermediate- to the low-energy regime.

The analysis of the entropy $S_\infty = \int_0^\infty dT(C/T)$ shows that the sum rule $S_\infty = k_B \ln 2$ per site is not satisfied in our result for $0 < p < 1$. Entropy is missing in our approximants: $\Delta S/S_\infty = 10\%$ for $p = 0.25$, 23% for $p = 0.5$, and 36% for $p = 0.75$. As our calculation methods provide reliable results down to $k_BT \sim J/5$, we expect that the missing entropy is "hidden" at lower temperatures. (Note that the specific heat decreases monotonically with increasing p for all temperatures $T > J/k_B$.) Thus a more careful discussion of the low-energy excitations and of the two regimes observed in the uniform susceptibility is necessary. In contrast to the classical limit it is not possible to introduce a well defined large correlation length $\tilde{\xi}(T)$ for the quantum system. Disorder in the quantum spin chain leads rather to an ensemble of FM and AF segments. Therefore, starting from high temperature, first correlation emerges among the spins within each segment separately. In a second step at lower temperature the segments begin to correlate among each other. This may be illustrated most easily for a nearly FM chain with a few isolated AF bonds. Each AF bond tends to lock its two adjacent spins into a singlet dimer and thereby decouple the long FM segments from each other. Therefore, as the spins align in each FM piece they act as one large spin. In this regime now the AF bonds act as barriers for the spin wave modes within each FM segment. As a consequence the contribution of these modes to the very low-energy spectrum is small, as we show in the following argument.

TABLE I. The exponent α as a function of p determined by a modified ratio method.

p	0.0	0.5	0.7	0.75	0.8	1.0
α	1	2.8 ± 0.6	3.3 ± 0.8	4.5 ± 1	5.7 ± 1	0.5

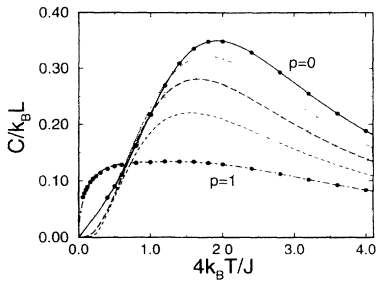

FIG. 3. Specific heat of the quantum spin chain for $p = 0$ (solid), 0.25 (dotted), 0.5 (long dashed), 0.75 (short dashed), and 1 (dash-dotted) obtained from two-point Padé approximation. The filled circles denote the results by Blöte for the uniform chains [6] and the empty circles the data of our transfer matrix calculation.

Assuming that the barriers are completely nontransparent the spin wave modes in each segment of length ℓ have a discrete spectrum $\omega_n(\ell) = (2\pi n/\ell)^2$ with $n = 1, 2, 3, \ldots$ (ω in units of Js). For very small $\varepsilon = 1 - p$ the probability to find a ferromagnetic segment of length ℓ is $\mathcal{P}(\ell) = \varepsilon \exp(-\varepsilon\ell)$. The corresponding density of states can be calculated using the optimal fluctuation scheme

$$\rho(\omega) = \int_0^\infty d\ell\, \mathcal{P}(\ell) \frac{1}{\ell} \sum_{n=1}^{\ell-1} \delta(\omega - \omega_n(\ell)) \sim \frac{\varepsilon}{4\omega} \frac{e^{-\pi\varepsilon/\sqrt{\omega}}}{\sinh(\pi\varepsilon/\sqrt{\omega})} \tag{7}$$

with $\omega \ll 1$. This density of states is exponentially suppressed with a pseudogap $\Delta \sim Js(2\pi\varepsilon)^2$. Additionally, in this picture the ground state is highly degenerate. While the suppression of the low-energy spin wave modes can account for the reduction in density of states [$\rho(\omega) \sim \omega^{\alpha-1}$] seen in our series expansion, the large degeneracy of the ground state contains the missing entropy, which can be estimated

$$\Delta S/k_B \sim \int_1^\infty d\ell\, \mathcal{P}(\ell) \frac{\ln(\ell)}{\ell} \sim \varepsilon \int_1^{1/\sqrt{2}\varepsilon} d\ell \frac{\ln(\ell)}{\ell} = \varepsilon(\ln \sqrt{2}\,\varepsilon)^2 \tag{8}$$

for $\varepsilon \to 0$. However, since the AF bonds create only finite potential barriers, the ground state degeneracy is lifted, and a band of excitation modes of the large spins appears. Consequently, we find a large density of states for very low lying excitations originating from intersegment correlations. These excitations should lead to a second (LT) peak structure in the specific heat at an energy scale lower than that due to the intrasegment excitations seen in

Fig. 3. Hence the missing entropy is absorbed in this peak which cannot be resolved within our calculation scheme. Note that our high-temperature expansion includes only correlations up to 11 lattice spacings while the properties of intersegment correlations exist on longer length scales. We can give a rough upper boundary for the position T_0 of the LT peak by the argument that the correlation length of the spins has to exceed the average segment length $\bar{\ell}$ to form a large spin, i.e., $\xi(T) \sim (J/k_BT)^{1/2} \sim \bar{\ell} = 1/\varepsilon$, which leads to $k_BT_0 \lesssim J\varepsilon^2 \sim \Delta$. For random chains of arbitrary p the approximate degeneracy of the ground state originates also from the existence of a larger FM piece separated by AF segments. As large FM segments are seldom for decreasing p the missing entropy in the HT peak shrinks. The intrasegment excitations for both the FM and AF segments are localized due to the fact that there is in general an energy-momentum mismatch for the modes impeding their transfer from one segment to the other (FM $\leftrightarrow$ AF). These excitations contribute little to the very low-energy spectrum as argued above for the nearly FM system. Therefore still the picture of the two different energy scales of the intrasegment and intersegment correlations should hold, leading to two peak structures in specific heat. Because of the formation of the large spins the susceptibility shows three regimes. Besides the HT regime with the standard Curie behavior, the large spins of the FM segments yield a new $1/T$ dependence of the susceptibility in an intermediate temperature regime ($T_0 < T < J/k_B$). In contrast to the classical spin system the susceptibility needs not be proportional to $1/T$ down to $T = 0$, but can even approach a finite value when the large spins eventually correlate among each other.

Our discussion suggests that the thermodynamic properties of the random quantum spin chain are determined by two energy scales visible in two peak structures of the specific heat. The LT $1/T$ behavior of the susceptibility of the classical systems probably appears only as an intermediate regime in the quantum spin chain. Our argumentation leads to the conclusion that the features found for the random $\pm J$-bond quantum spin chain are typical for a wider class of spin systems with discrete bond disorder. Therefore it may apply to some of the systems mentioned in the introduction so that our picture can be tested experimentally.

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