Impurities in $S = 1/2$ Heisenberg Antiferromagnetic Chains: Consequences for Neutron Scattering and Knight Shift

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Nonmagnetic impurities in an $S = 1/2$ Heisenberg antiferromagnetic chain are studied using boundary conformal field theory techniques and finite-temperature quantum Monte Carlo simulations. We calculate the static structure function, $S_{\rm imp}(k)$, measured in neutron scattering and the local susceptibility, χ_i measured in Knight shift experiments. $S_{\rm imp}(k)$ becomes quite large near the antiferromagnetic wave vector, and exhibits much stronger temperature dependence than the bulk structure function. χ_i has a large component which alternates and *increases* as a function of distance from the impurity.

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Although the spin chain problem has been a popular topic for theoretical physicists since the early days of quantum mechanics, the correlation functions of the antiferromagnetic Heisenberg spin-1/2 chain could only be calculated with the help of modern quantum field theory [1]. Adding nonmagnetic impurities to a spin-chain compound breaks the chains up into finite sections with essentially free boundary conditions. The correlation functions in the presence of such a boundary were calculated only recently [2]. These results provide a simple application of a general theory of conformally invariant boundary conditions which has been applied to a wide variety of quantum impurity problems in condensed matter and particle physics [3]. These functions exhibit a universal dependence on the boundary, at long distances and times. In this paper we wish to focus on a couple of applications to these results of experimental relevance: the impurity contribution to the static structure function, $S_{\rm imp}(k, T)$, and the local susceptibility, $\chi_i(T)$. We derive analytic expressions for these quantities using field theory methods and compare them with finite-T Monte Carlo simulations using lengths of up to $l = 128$ with a varying number of time steps up to 64 and several hundred thousand sweeps through each lattice.

The Heisenberg Hamiltonian for the antiferromagnetic spin-1/2 chain

$$H = J \sum_i \vec{S}_i \cdot \vec{S}_{i+1} \tag{1}$$

is equivalent to a free boson field theory in 1+1 dimensions in the low energy, long-distance limit [4]. The spin operators are expressed in terms of the boson ϕ as

$$S^z_j \approx \partial_x \phi/\sqrt{2\pi} + a(-1)^j \cos\sqrt{2\pi}\phi\,, \tag{2}$$

where a is a constant. The boson Hamiltonian is then simply given by the free part together with terms which become irrelevant as the temperature is lowered. Those irrelevant terms give rise to temperature and finite length dependent corrections with a characteristic power law.

This theory has been used successfully to calculate impurity effects [2], the low energy spectrum [5], and correlation functions [1]. The latter agree well with recent neutron scattering experiments [6]. Like the expression for the spin operators in Eq. (2), the correlation functions also acquire an alternating and a uniform part as a function of the site index x. At finite temperature, the alternating part is given by

$$\langle S^z(x,t_1)S^z(y,t_2)\rangle_{\rm alt} \to c\frac{\pi}{v\beta}\frac{(-1)^{x-y}}{\sqrt{\sinh[\pi(x-y-v\Delta t)/v\beta]\sinh[\pi(x-y+v\Delta t)/v\beta]}}\,, \tag{3}$$

($\Delta t \equiv t_2 - t_1$). We set the lattice spacing to 1. The spin-wave velocity is known to be $v = J\pi/2$ from the Bethe ansatz. The constant c can be determined numerically and is given by $c = a^2/2$ times an arbitrary normalization of the two-point function, which we chose to set to 1. The irrelevant terms in the Hamiltonian give logarithmic corrections to this expression [5]. In fact, it has been shown recently that the logarithmic corrections give rise to an infinite slope of the uniform susceptibility at zero temperature [7].

The correlation functions in the presence of a boundary were first calculated in Ref. [2]. There it was argued that the free boundary condition on the spin operators corresponds, in the continuum limit, to a boundary condition on the bosons: $\phi(0) = \phi_L(0) + \phi_R(0) = \sqrt{\pi/8}$. Since ϕ_L is a function only of $vt + x$ and ϕ_R of $vt - x$, this

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implies that we may simply regard this boundary condition as defining ϕ_R to be the analytic continuation of ϕ_L to the negative axis $\phi_R(x) = -\phi_L(-x) + \sqrt{\pi/8}$. Whereas the bulk correlation function factorizes into a product of left and right two-point Green's functions, the boundary correlation function becomes a four-point Green's function for left-movers. Consequently, while the uniform part is largely unaffected by an open boundary condition, the alternating part gets modified to

$$c(-1)^{x-y}\frac{\pi}{v\beta}\Bigg[\sinh\frac{2\pi x}{v\beta}\sinh\frac{2\pi y}{v\beta} \times\left(\sinh\frac{\pi(x+y+v\Delta t)}{v\beta}\sinh\frac{\pi(x+y-v\Delta t)}{v\beta}\sinh\frac{\pi(x-y+v\Delta t)}{v\beta}\sinh\frac{\pi(x-y-v\Delta t)}{v\beta}\right)^{-1}\Bigg]^{1/2}, \tag{4}$$

which reduces to Eq. (3) in the bulk limit $xy \gg |(x-y)^2 - v^2\Delta t^2|$.

Here we have also included the time dependence of the Green's function, but we will only calculate the equal-time spatial Fourier transform $S(k)$, deferring consideration of the full dynamical structure function to later work. We predict a characteristic impurity contribution to the structure factor, which may be observable in magnetic neutron scattering experiments on quasi-one-dimensional spin-1/2 magnetic compounds (e.g., $KCuF_3$). Doping with impurities will break the spin chains and thereby introduce the desired open ends. For a finite chain of length l we can define a structure factor $S_l(k)$ as

$$S_l(k) \equiv \frac{1}{l}\sum_{x,y=1}^{l}\langle S^z(x)S^z(y)\rangle e^{ik(x-y)} \xrightarrow{l\to\infty} S(k) + \frac{S_{\rm imp}(k)}{l}. \tag{5}$$

The structure function for the finite chains has been decomposed into a "bulk" part $S(k)$ which is independent of length and an "impurity" part of order $1/l$: $S_{\rm imp}(k) \equiv \lim_{l\to\infty} l[S_l(k) - S(k)]$. The bulk part reproduces the signal of a system without open ends (e.g., an infinite chain) while the effect of the open boundary condition is entirely contained in the impurity part. Higher order $\mathcal{O}(1/l^2)$ terms will also be present, but can be neglected if the impurities are dilute. Since each impurity creates the same contribution $S_{\rm imp}(k)$ in the dilute limit, the experimental signal will contain the impurity part as a term that scales with impurity concentration n to first order: $S_{\rm exp}(k) \approx S(k) + nS_{\rm imp}(k)$.

From the results of Eqs. (3) and (4), it is clear that we expect interesting effects for wave vectors near $k \approx \pi$. Field theory predictions for small $k - \pi$ and T are obtained by Fourier transforming Eqs. (3) and (4). We assume here that the impurities are dilute enough so that the infrared cutoff is always given by the inverse temperature $\beta \ll l/v$. The bulk structure function [8] can then be expressed in terms of the digamma function ψ [9] and the reduced variable $k' \equiv (k-\pi)v\beta/\pi$:

$$S(k') = 2c[\ln(\Lambda\beta J) - \mathrm{Re}\,\psi(1/2 - ik'/2)], \tag{6}$$

where Λ is a constant depending on the cutoff.

The impurity contribution $S_{\rm imp}(k')$ is obtained by Fourier transforming Eq. (4) with the bulk part, from Eq. (3), subtracted off assuming two open ends. This subtraction eliminates the ultraviolet divergence, giving the scaling form

$$S_{\rm imp}(k') = c\frac{2v\beta}{\pi}\int_0^\infty dw\Bigg[\int_0^w du\frac{\cos k'u}{\sinh u}\times\left(\sqrt{1-\frac{\sinh^2 u}{\sinh^2 w}}-1\right) - \int_w^\infty du\frac{\cos k'u}{\sinh u}\Bigg] = v\beta f(k'). \tag{7}$$

Here $u = \pi(x-y)/v\beta$, $w = \pi(x+y)/v\beta$. Note that, apart from the logarithmic term in Eq. (6), $S(k')$ and $S_{\rm imp}(k')$ are functions only of the scaling variable k', but we expect corrections from irrelevant operators and the finite ultraviolet cutoff which become smaller as $T \to 0$ and $(k-\pi) \to 0$, with k held fixed. For small k' we have $S(k') \propto \ln(\beta) + \text{const} + \mathcal{O}(k'^2)$ and $S_{\rm imp}(k') \propto v\beta[\text{const} + \mathcal{O}(k'^2)]$, so that the impurity part has a much stronger temperature dependence. At large k', $S(k')$ vanishes exponentially, but $S_{\rm imp}(k') \to -v\beta c/\pi k'^2$.

Our Monte Carlo results for $S(k)$ and $S_{\rm imp}(k)$ are shown in Figs. 1 and 2 for four different temperatures. To

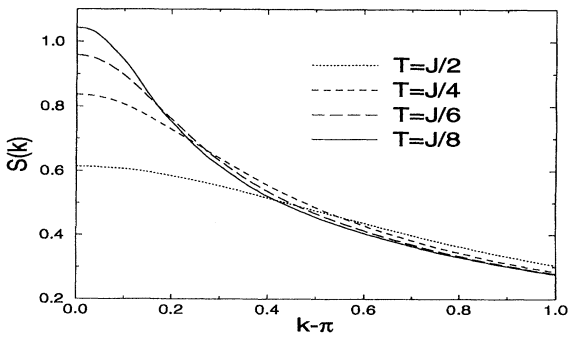

FIG. 1. The bulk structure factor $S(k)$ according to quantum Monte Carlo simulations.

show the predicted scaling form we plotted the results as a function of the reduced variable k' in Figs. 3 and 4. The Monte Carlo simulations agree reasonably well with the field theory predictions. This comparison with the Monte Carlo data was used to extract the constant $c = 0.14$ and $\Lambda = 0.75$ in Eq. (6).

We now consider the local susceptibility χ_i at any arbitrary site i under the influence of a uniform magnetic field h acting on the complete chain

$$\chi_i(T) \equiv \frac{\partial}{\partial h}\langle S_i^z\rangle \Big|_{h=0} = \frac{1}{T}\sum_j \langle S_j^z S_i^z\rangle . \tag{8}$$

For a chain with periodic boundary conditions, χ_i is the same for all sites because of translational invariance.

If we are dealing with an open boundary condition, however, the translational invariance is clearly broken and we would naively expect the open end to be more susceptible. Moreover, it is now possible, in the field theory treatment, to have a nonzero alternating susceptibility as a function of site index $\chi_x = \chi_x^{\rm uni} + (-1)^x \chi_x^{\rm alt}$. Using the analytic continuation of the left-movers onto the negative half axis from above, $\chi_x^{\rm alt}$ is given by a nonzero three-point Green's function:

$$\begin{aligned}\chi_x^{\rm alt} &\equiv \beta\left\langle S^z_{\rm alt}(x)\int_{-\infty}^{\infty} dy\, S^z_{\rm uni}(y)\right\rangle = \frac{a\beta}{\sqrt{8\pi}}\int_{-\infty}^{\infty} dy\left\langle ie^{-i\sqrt{2\pi}\phi_L(x,t')}e^{i\sqrt{2\pi}\phi_L(-x,t')}\frac{\partial\phi_L}{\partial x}(y,t) + \text{H.c.}\right\rangle \\ &= \frac{a\beta}{4\pi}\int_{-\infty}^{\infty} dy \frac{\sqrt{(v\beta/\pi)\sinh(2\pi x/v\beta)}}{(v\beta/\pi)\sinh[\pi(y+x+iv\Delta\tau)/v\beta](v\beta/\pi)\sinh[\pi(y-x+iv\Delta\tau)/v\beta]} \\ &= \frac{a}{v}\frac{x}{\sqrt{(v\beta/\pi)\sinh(2\pi x/v\beta)}},\end{aligned} \tag{9}$$

where x is the distance from an open boundary condition. At low temperatures the alternating part actually *increases* with the distance from the open end $\chi_x^{\rm alt} \xrightarrow{\beta\to\infty} a\sqrt{x}/\sqrt{2}v$. Any finite temperature suppresses this growth exponentially with x, so that we expect a typical maximum which gets shifted further into the chain as the temperature is lowered. Furthermore, even at $T = 0$, the staggered magnetization does not increase indefinitely with distance from the impurity, but rather oscillates with a wavelength, $4\pi v/h$, i.e., $M^{\rm alt}(x, h, T = 0) = a\sqrt{2/x}\,\sin(hx/2v)$. This exotic behavior is similar to Friedel oscillations except that the $1/r^3$ decay, which occurs there, gets enhanced to a $\sqrt{r}$ *growth* due to a combination of reduced dimensionality and the absence of charge fluctuations in this pure spin system.

The result from Eq. (9) can be confirmed independently with quantum Monte Carlo simulations. The local susceptibility as a function of distance from the open end is shown in Fig. 5 from Monte Carlo simulations at $T = J/15$. After extracting the uniform and alternating parts as shown in Fig. 6, we can compare the alternating part to the predicted form from Eq. (9), where the overall constant was chosen to be $a = 0.58$. The field theory prediction, $c = a^2/2$, together with the value $c = 0.14$ from our MC measurement of $S(k)$, gives $a \approx 0.53$, in reasonable agreement with above. While the shape of the theoretical prediction for $\chi_x^{\rm alt}$ fits the Monte Carlo results very well, there is an unexplained shift of about two sites, which might be due to irrelevant operators. The functional dependence in Eq. (9) holds rather well for all temperatures β sampled (up to the shift of two sites). For $T = J/15$ the shift in the susceptibility due to the impurity is larger than the bulk susceptibility over a distance of about 25 lattice sites from the impurity. Thus we expect that it should be possible to observe this effect in nuclear magnetic resonance Knight shift experiments. Note that $\chi_i < 0$ for small even i, so that those spins will tend to antialign with the applied field.

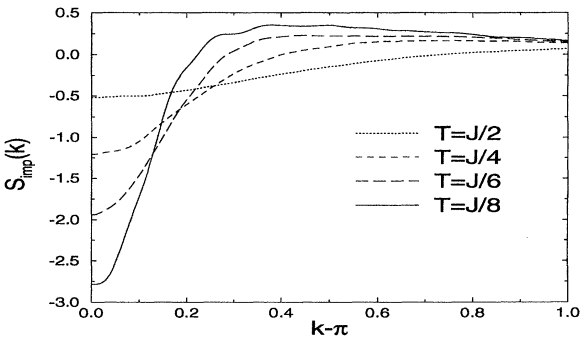

FIG. 2. The impurity part of the structure factor $S_{\rm imp}(k)$ according to quantum Monte Carlo simulations.

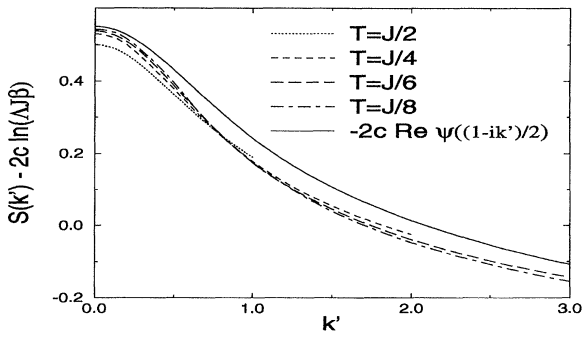

FIG. 3. Monte Carlo results for the shifted bulk structure function, $S(k') - 2c\,\ln(\Lambda J\beta)$, compared to the field theory prediction of Eq. (6), with $c = 0.14$ and $\Lambda = 0.75$.

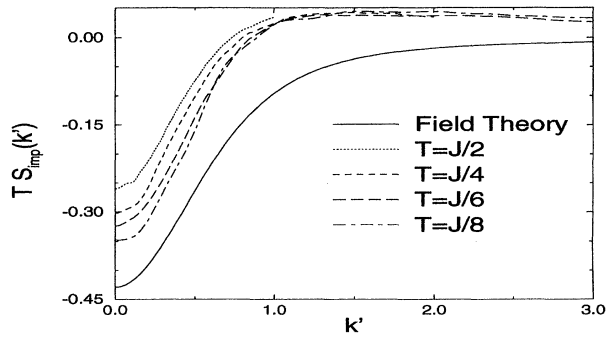

FIG. 4. Monte Carlo results for the scaled impurity part $TS_{\rm imp}(k')$ compared to Eq. (7) with $c = 0.14$.

The uniform part of the susceptibility is not directly affected by the boundary condition, but gets an additional nonuniversal contribution near $x = 0$ from an irrelevant boundary operator [2,10], which also appears to be present in the Monte Carlo results in Fig. 6. This shift in the uniform susceptibility is what would be expected classically, but the large alternating part is a purely quantum mechanical effect.

In conclusion, we have calculated the effect of impurities on the neutron scattering cross section and the NMR Knight shift using both field theory and Monte Carlo methods. The two methods are in reasonable agreement and the effects seem large enough to be observable experimentally. The Knight shift actually *increases* with distance from the impurity in the limit of zero field and temperature.

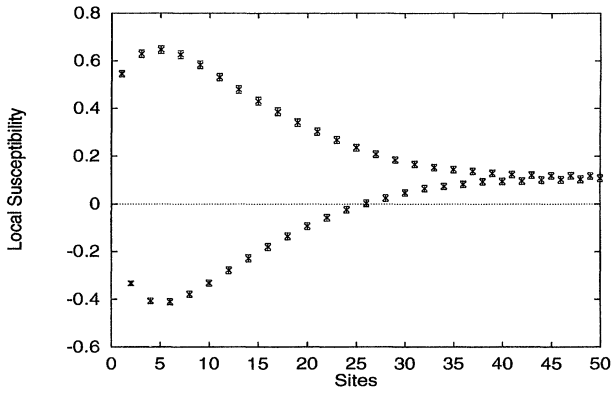

FIG. 5. The local susceptibility vs distance from the open end according to Monte Carlo simulations at $T = J/15$.

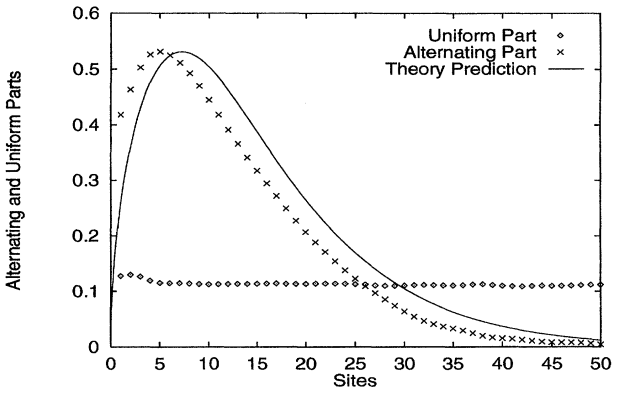

FIG. 6. The uniform and alternating parts of the local susceptibility according to Monte Carlo simulations at $T = J/15$ compared to the field theory equation (9) with $a = 0.58$.

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