Boundary Susceptibility in the Spin-1/2 Chain: Curie-Like Behavior without Magnetic Impurities

Satoshi Fujimoto[1] and Sebastian Eggert[2]

[1]*Department of Physics, Kyoto University, Kyoto 606-8502, Japan*

[2]*Institute of Theoretical Physics, Chalmers University of Technology, S-41296 Göteborg, Sweden*

(Received 7 October 2003; published 23 January 2004)

We investigate the low-temperature thermodynamics of the spin-1/2 Heisenberg chain with open ends. On the basis of boundary conformal field theory arguments and numerical density matrix renormalization group calculations, it is established that in the isotropic case the impurity susceptibility exhibits a Curie-like divergent behavior as the temperature decreases, even in the absence of magnetic impurities. A similar singular temperature dependence is also found in the boundary contributions of the specific heat coefficient. In the anisotropic case, for $1/2 < \Delta < 1$, these boundary quantities still show a singular temperature dependence obeying a power law with an anomalous dimension. Experimental consequences will be discussed.

DOI: 10.1103/PhysRevLett.92.037206 PACS numbers: 75.10.Jm, 75.20.Hr

Impurity doping in low dimensional antiferromagnetic systems has been a topic of great interest in recent years [1–11]. New interesting boundary phenomena give better physical insight into the underlying structure of the strongly correlated states in those systems. In one-dimensional systems impurities typically cut the chains and play the role of effective boundary conditions. The open ends give rise to intriguing boundary phenomena, which result in a characteristic temperature dependence of the excess susceptibility and specific heat due to the impurities. Famous examples include the spin-1 chain where effective spin-1/2 degrees of freedom are created near the open ends which show clear experimental signatures [1]. Even in the two-dimensional Heisenberg model it has been postulated that nonmagnetic impurities may give rise to a divergent Curie-like impurity susceptibility [2]. However, the temperature dependence of the boundary susceptibility has been much less clear in the case of the antiferromagnetic spin-1/2 chain, which is possibly the oldest and most studied prototype of a strongly correlated system. According to the Bethe ansatz solutions for integrable systems with open boundaries, the boundary part of the uniform spin susceptibility at zero temperature behaves like $\sim 1/[h\{\ln(h)\}^2]$ for a small magnetic field h in the case of SU(2) spin rotational symmetry [3–6]. This divergent behavior implies that in the vicinity of the open edges spin excitations are very sensitive to small external fields. It seems therefore likely that the susceptibility should also show divergent behavior for small temperatures at zero field. On the other hand, irrelevant boundary operators are known to produce only a small finite impurity susceptibility at low temperatures [7]. We now show that an addition to the surface energy from the marginally irrelevant bulk operator actually gives rise to the leading singular temperature behavior of the impurity susceptibility and the specific heat coefficient corresponding to a Curie-like behavior with logarithmic corrections.

We consider the antiferromagnetic spin-1/2 Heisenberg chain with open boundaries

$$H_{XXZ} = J \sum_{i=1}^{N} [S_i^x S_{i+1}^x + S_i^y S_{i+1}^y + \Delta S_i^z S_{i+1}^z] \qquad (1)$$

in the limit $N \gg J/T$, i.e., the thermodynamic limit. Note that in the opposite limit $T/J \ll 1/N$ the behavior is trivially described by the ground state, which is a singlet for even N with exponentially small susceptibility as $T \to 0$ and a doublet for odd N with a Curie law behavior. The crossover to the ground state behavior is experimentally important and will be discussed later, but for now we will consider the low-temperature behavior in the thermodynamic limit $1/N \ll T/J \ll 1$. In the massless region, $0 \le \Delta \le 1$, the low-energy fixed point of the Hamiltonian (1) is the Tomonaga-Luttinger liquid, which belongs to the universality class of the Gaussian theory with the central charge $c = 1$. The low-energy effective Hamiltonian with leading irrelevant interactions has been exactly obtained by Lukyanov [12]. Using this effective theory we can implement a perturbative expansion of the free energy in terms of leading irrelevant interactions and evaluate impurity corrections of order $1/N$. Following the idea of Cardy and Lewellen [13], we consider a semi-infinite cylinder on which the direction tangent to the circumference is taken as an imaginary time axis and the direction perpendicular to it as a space axis. The circumference is equal to the inverse temperature $1/T$. We define the boson phase field on this geometry, of which the mode expansion is given by

$$\phi^c(x,\tau) = Q - i\pi TPx + 2\pi T \frac{w\tau}{\sqrt{2K}} + \frac{i}{2} \sum_{n \neq 0} \frac{1}{n} (\alpha_n e^{-2\pi Tn(x+i\tau)} + \bar{\alpha}_n e^{-2\pi Tn(x-i\tau)}), \qquad (2)$$

where w is the winding number of ϕ^c, K is the Luttinger

liquid parameter, and the operators satisfy the commutation relations $[\alpha_n, \alpha_m] = [\bar{\alpha}_n, \bar{\alpha}_m] = n\delta_{n+m,0}$, $[\alpha_n, \bar{\alpha}_m] = 0$, and $[Q, P] = i$. Then, the low-energy effective Hamiltonian on the semi-infinite cylinder is written as

$$H^c = H_0^c + H_{\rm int}^c, \tag{3}$$

$$H_0^c = \int_0^{1/T} \frac{d\tau}{2\pi}[(\partial_\tau \phi^c)^2 + (\partial_x \phi^c)^2], \tag{4}$$

$$H_{\rm int}^c = -a^{2K-2}\lambda \int_0^{1/T} \frac{d\tau}{2\pi} \cos(\sqrt{8K}\phi^c). \tag{5}$$

Here the constants K and a are parametrized as $K = [1 - (1/\pi)\cos^{-1}(\Delta)]^{-1}$, $a = 2(K-1)/[JK\sin(\pi/K)]$, and λ is given by Eq. (2.24) in Ref. [12]. For this choice of the lattice parameter a, the velocity of spinons is unity in the unit of $1/a$. Thus the Hamiltonian (3) is obtained by simply interchanging time and space coordinates of the usual Hamiltonian defined on a circumference of $L = aN$.

We express the partition function by using the transfer matrix $\exp(-LH^c)$ and the boundary state for H_0^c, $|B\rangle$. The lowest order terms of the free energy for the Hamiltonian (3) are given by

$$F = -\frac{aT}{L}\ln\langle 0|e^{-LH_0^c}|B\rangle + \frac{aT}{L}\int_0^L dx \frac{\langle 0|\exp(-LH_0^c)\exp(xH_0^c)H_{\rm int}^c \exp(-xH_0^c)|B\rangle}{\langle 0|\exp(-LH_0^c)|B\rangle} + \cdots, \tag{6}$$

where $|0\rangle$ is the ground state of H_0^c. The first term on the right-hand side of Eq. (6) is the free energy of the $c = 1$ Gaussian model. The second term is the $1/L$ correction that emerges as a result of boundary effects. For the periodic boundary condition, this term vanishes. In the case of an external magnetic field h, the free energy is evaluated by shifting the boson field $\phi^c(x)$ to $\tilde{\phi}^c(x) = \phi^c(x) - \sqrt{K/2}hx$. Using the Cardy-Lewellen method [13], we compute the first order term as

$$-\frac{\lambda}{L}\frac{(\pi a T)^{2K}}{2\pi a}\frac{\langle \Phi \mid B\rangle}{\langle 0 \mid B\rangle}\int_0^L dx \frac{\cos(2Khx)}{[\sinh(2\pi T x)]^{2K}}, \tag{7}$$

where $|\Phi\rangle$ is the primary state that corresponds to the conformal field $\exp(i\sqrt{8K}\phi^c)$. In the following, we evaluate Eq. (7) exactly for the free open boundary condition.

To calculate the prefactor in Eq. (7), we utilize properties of the boundary state. A conformally invariant boundary condition is imposed by demanding $T(z) = \bar{T}(\bar{z})$ at the boundary [14]. Here $T(z)$ $[\bar{T}(\bar{z})]$ is the holomorphic (antiholomorphic) part of the stress energy tensor. For the Gaussian model with $c = 1$, this condition leads to the following constraint on the boundary state [15–17]:

$$(\alpha_n \pm \bar{\alpha}_{-n})|B\rangle = 0, \tag{8}$$

where the plus (minus) sign corresponds to the Neumann (Dirichlet) boundary condition. Equation (8) is solved in terms of the Ishibashi states, which, in our case, are constructed from the highest weight states of the U(1) Kac-Moody algebra $|v, w\rangle$ and their descendants [18]. Here v, w are integers specifying the U(1) highest weight state. The leading irrelevant interaction (5) is expressed by the primary field $\exp(i\sqrt{8K}\phi^c)$ which corresponds to the primary state $|2, 0\rangle$. Therefore, $\langle \Phi \mid B\rangle$ is nonvanishing, only if $|B\rangle$ contains $|2, 0\rangle$. The Neumann boundary state which consists of the highest weight state $|0, w\rangle$ and its descendants does not satisfy this condition. On the other hand, the Dirichlet boundary state,

$$|D\rangle = \left(\frac{K}{2}\right)^{1/4} \sum_{v=-\infty}^{\infty} e^{-i\sqrt{2K}v\phi_0} e^{-\sum_{n=1}^{\infty}\alpha_{-n}\bar{\alpha}_{-n}/n}|v, 0\rangle, \tag{9}$$

has a finite overlap with $|\Phi\rangle$. Then, we have

$$\frac{\langle 2, 0 \mid D\rangle}{\langle 0 \mid D\rangle} = 1. \tag{10}$$

Carrying out the integral in Eq. (7) and using Eq. (10), we obtain corrections to the boundary part of the free energy,

$$\delta F_{\rm B} = -\frac{\lambda}{2\pi a N}(2\pi a T)^{2K-1} \times {\rm Re}\left[B\left(K + i\frac{Kh}{2\pi T}, 1 - 2K\right)\right], \tag{11}$$

where $B(x, y) = \Gamma(x)\Gamma(y)/\Gamma(x + y)$.

The boundary contribution to the spin susceptibility is derived from Eq. (11),

$$\chi_{\rm B} = \frac{\lambda a K^2}{2\pi N} B(K, 1 - 2K)[\pi^2 - 2\psi'(K)](2\pi a T)^{2K-3}, \tag{12}$$

with $\psi'(x) = d\psi(x)/dx$. Note that for $1 < K < 3/2$ $(1/2 < \Delta < 1)$, the boundary spin susceptibility $\chi_{\rm B}$ shows a divergent behavior $\sim 1/T^{3-2K}$, as temperature decreases. This anomalous temperature dependence is also observed in the boundary part of the specific heat coefficient computed as

$$\frac{C_{\rm B}}{T} = \frac{2\pi a \lambda}{N}(2K - 1)(2K - 2)B(K, 1 - 2K)(2\pi a T)^{2K-3}. \tag{13}$$

Boundary terms that are regular in h and T give higher order corrections and have been neglected here. We would like to stress that in the formulas (12) and (13) there is no free parameter, and the prefactors are exact. The divergent behaviors of Eqs. (12) and (13) for $T \to 0$ are physically understood as follows. In contrast to the bulk Heisenberg chains, the ground state degeneracy at the boundaries gives rise to large spin fluctuations, which disturb the spin singlet formation. It should be emphasized that the singular behaviors are not due to the presence of boundary operators, but interpreted as a consequence of

finite-temperature corrections of the surface energy and the boundary entropy $\ln\langle 0 \mid B\rangle$ caused by bulk irrelevant interactions.

At zero temperature with a small magnetic field, a similar singular behavior appears in the field dependence of the boundary spin susceptibility given by

$$\chi_{\mathrm{B}}(T=0) = \frac{\lambda(aK)^{2K-1}}{2\pi a N}\sin(\pi K)\Gamma(3-2K)h^{2K-3}. \quad (14)$$

The zero temperature susceptibility is also derived from the Bethe ansatz exact solution by using the Wiener-Hopf method. We have checked that Eq. (14) coincides with the result obtained by the Bethe ansatz method.

Now let us consider the isotropic case $K = 1$. The free energy correction (11) possesses poles for $K = 1$. To deal with these singularities, we follow the procedure considered by Lukyanov for bulk spin systems [12]. We rewrite H_{int} in terms of the SU(2) current operators,

$$H_{\mathrm{int}} = \int \frac{dx}{2\pi}\left[g_{\parallel} J_0 \bar{J}_0 + \frac{g_{\perp}}{2}(J_+\bar{J}_- + J_-\bar{J}_+)\right]. \quad (15)$$

The exact expressions for the running coupling constants are known as $g_{\parallel} = 2(1-1/K)(1+q)/(1-q)$, $g_{\perp} = 4(1-1/K)q^{1/2}/(1-q)$ [12,19]. Here the parameter q is the function of T and h, of which the expression is also known exactly. On the other hand, for the value of K close to 1, Eq. (11) can be expanded in a power series of $1-1/K$. Comparing the expansion of Eq. (11) with the expression for $g_{\parallel}$ and $g_{\perp}$, we can write the free energy correction (11) as a power series expansion in terms of $g_{\parallel}$ and $g_{\perp}$. Then, taking the limit $K \to 1$ and $g_{\parallel}, g_{\perp} \to g$, we end up with

$$\delta F_{\mathrm{B}} = -\frac{Tg}{2N} - \frac{h^2}{24NT}(g+g^2) + \cdots \quad (16)$$

for $h \ll T$. The running coupling constant is determined from the equation

$$g^{-1} + \frac{1}{2}\ln(g) = -\mathrm{Re}\left[\psi\left(1+\frac{ih}{2\pi T}\right)\right] + \ln\left(\sqrt{\frac{\pi}{2}}\frac{e^{1/4}J}{T}\right), \quad (17)$$

where $\psi(x)$ is the di-gamma function. Using Eqs. (16) and (17), we obtain the leading term of the boundary spin susceptibility and the specific heat coefficient,

$$\chi_{\mathrm{B}} = \frac{g}{12NT} + \frac{g^2}{12NT}\left(1 - \frac{3\psi''(1)}{2\pi^2}\right) + \cdots = \frac{1}{12NT\ln(\alpha/T)}\left(1 - \frac{\ln\ln(\alpha/T)}{2\ln(\alpha/T)} + \cdots\right), \quad (18)$$

$$\frac{C_{\mathrm{B}}}{T} = \frac{g^2}{2NT} + \frac{5g^3}{4NT} + \cdots = \frac{1}{2NT(\ln(\alpha/T))^2}\left(1 - \frac{\ln\ln(\alpha/T)}{\ln(\alpha/T)} + \cdots\right), \quad (19)$$

where $\alpha = \sqrt{\pi/2}\exp(1/4+\gamma)$ with γ the Euler constant. At zero temperature, the boundary spin susceptibility for a small magnetic field is also derived from the opposite limit $h \gg T$ of Eq. (11),

$$\chi_{\mathrm{B}}(T=0) = \frac{g^2}{4Nh} + \frac{5g^3}{8Nh} + \cdots = \frac{1}{4Nh(\ln(2\pi\alpha/h))^2}\left(1 - \frac{\ln\ln(2\pi\alpha/h)}{\ln(2\pi\alpha/h)} + \cdots\right). \quad (20)$$

This result (20) coincides completely with that obtained by the Bethe ansatz exact solutions [3–6].

The prefactor of the leading terms in Eqs. (18)–(20) are exact for the isotropic Heisenberg chain, but not universal. For example a frustrating nearest neighbor coupling J_2 will change the prefactors and at the critical point $J_2 \approx 0.241167$ [20] the singular behavior is absent. Special logarithmic singularities at boundaries have also been found in the NMR relaxation rate [8,9], which are also directly related to the bulk marginal operator. However, in Eqs. (18) and (19) it is even the leading T dependence that is changed due to this irrelevant operator.

For comparison we have also used the numerical density matrix renormalization group for transfer matrices (TMRG) applied to impurity problems [10]. This method can calculate local expectation values and the impurity free energy directly in the thermodynamic limit $N \to \infty$. When evaluating the impurity susceptibility we need to take the second derivative of the impurity free energy and therefore subtract two large numbers, which becomes inaccurate for very low temperatures. For the lowest temperatures ($T < 0.1J$) we have instead summed over the excess local responses in a range around the open ends, which gave more accurate results. This method agrees with taking the second derivative for higher T and should also be a good approximation for $T < 0.1J$. Note, however, that taking the excess response only at the site closest to the open end as was done in Ref. [10] gives a weaker temperature dependence. The results are shown in Fig. 1 without any adjustable parameters.

Finally, we would like to remark on the implications of our findings for experimental observations. In experimental quasi-one-dimensional systems such as Sr_2CuO_3 a small density ρ of impurities is always present in the form of intrinsic defects of the crystal which effectively cut the chains. A corresponding Curie contribution has been observed that can be strongly reduced by careful annealing [21,22], which implies that this Curie tail cannot be due to magnetic impurities in the sample. For extremely low temperatures $T/J \ll 1/N$ such a Curie behavior can be explained by finite chains with odd N that have locked into their doublet ground state [11]. We have now shown that a Curie-like behavior can even be

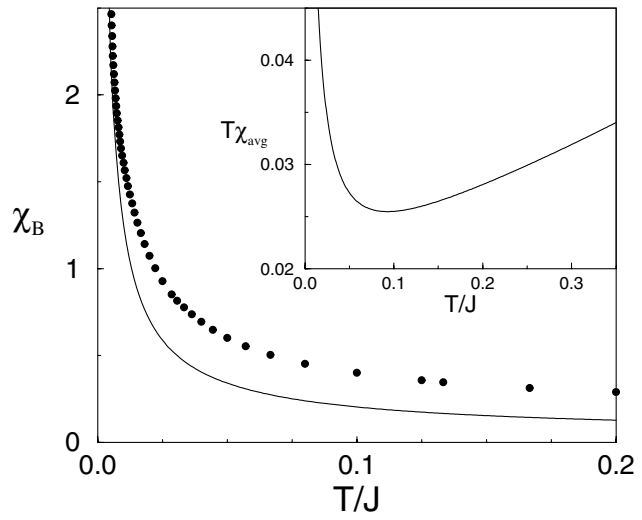

FIG. 1. The boundary susceptibility χ_B as a function of T according to the DMRG calculations (black points), compared to the result of the field theory in Eq. (18). Inset: approximate temperature dependence of the average Curie constant per impurity for an impurity density of $\rho = 0.1\%$

expected for higher temperatures, albeit with a different Curie constant in Eq. (18). The crossover between the ground state and the thermodynamic behavior is well understood, and in fact the partition function can be written explicitly if irrelevant operators are ignored [7]. Roughly, the crossover occurs when the temperature becomes comparable to the finite size energy gap $T \sim \pi v/N$. For a carefully annealed sample of Sr_2CuO_3 with $\rho \sim 0.013\%$ [21] this means that the ground state contribution is significant only for $T \lesssim 0.001J \sim 2$ K. For higher temperatures the impurity susceptibility is dominated by the expression in Eq. (18). Experimentally this means that the effective Curie constant first drops logarithmically as the temperature is lowered. In previous studies this slight change of the Curie constant has been fitted to a Curie-Weiss correction [22] assuming a phenomenological interaction between the impurity moments. The result in Eq. (18) now gives a clear prescription for the expected form of the impurity susceptibility. At the lowest temperatures $T \lesssim 5\rho J$, the Curie constant increases again sharply to a limiting value of $\rho/8J$ as $T \to 0$ due to the ground state contributions of the chains with odd N [11], leading to a characteristic minimum in the average Curie constant $T\chi_{avg}$. The approximate behavior of the averaged impurity susceptibility $T\chi_{avg}$ is shown in the inset of Fig. 1 for $\rho = 0.1\%$ by averaging over all chain lengths and assuming a sharp crossover from ground state to thermodynamic behavior.

In summary, we have studied the boundary thermodynamics for spin-1/2 Heisenberg chains with open ends by using boundary conformal field theory and numerical TMRG calculations. It has been shown that the boundary contributions of the spin susceptibility and the specific heat coefficient exhibit divergent behaviors as the temperature is lowered, which explains experimental observations in quasi-one-dimensional compounds.

We would like to thank I. Affleck, F. H. L. Essler, and N. Kawakami for valuable discussions. We are also grateful to A. Furusaki for sharing his insight about related issues which led us to find an error in an earlier version of the formula (18). This work was partly supported by a Grant-in-Aid from the Ministry of Education, Science, Sports and Culture, Japan and the Swedish Research Council.

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