Realization of a Witten Critical Theory in $(CH_3)_4NMnCl_3$

Ian Affleck

Joseph Henry Laboratories, Princeton University, Princeton, New Jersey 08544

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The exact $T=0$ susceptibility times spin-wave velocity of an isotropic spin-s antiferromagnetic chain is calculated by use of the Wess-Zumino-Witten σ model, with Kac-Moody central charge $k=2s$, as the critical theory. The result, $\chi v_s = k/2\pi$, agrees exactly with Bethe-*Ansatz* results for integrable models and well with numerical results ($s=\frac{1}{2}$), Fisher's classical limit, and experiments on $CuCl_2 \cdot 2NC_5H_5$ ($s=\frac{1}{2}$) and $(CH_3)_4NMnCl_3$ ($s=\frac{5}{2}$). ($\chi_\parallel$ is also calculated exactly for $s=\frac{1}{2}$ and arbitrary planar anisotropy.) This suggests that $(CH_3)_4NMnCl_3$ is an experimental realization of this new universality class.

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It has been known for some time[1] that the low-energy, critical properties of massless quantum antiferromagnetic chains are given by $(1+1)$-dimensional relativistic quantum field theories with the spin-wave velocity v_s being the effective velocity of light. Thus their zero-temperature (T) behavior is that of two-dimensional classical systems at finite T. The $s=\frac{1}{2}$ system with Hamiltonian

$$H=\sum_i [S_i^x S_{i+1}^x + S_i^y S_{i+1}^y + \Delta S_i^z S_{i+1}^z] \quad (1)$$

is in the same universality class as the two-dimensional classical xy model. It was argued elsewhere[2,3] that isotropic systems ($\Delta=1$) of higher half-integer spin belong to new universality classes that have not yet been seen in two dimensions. These are conformally invariant nonlinear σ models, discovered by Witten,[4] which have Wess-Zumino topological terms with integer coupling constant, k. Alternatively, they can be viewed as representations of the SU(2) Kac-Moody algebra with central charge, k. It was argued[2,3] that the critical theory for half-integer s is the Wess-Zumino-Witten (WZW) model with $k=2s$. [Integer-s chains with the quadratic Hamiltonian of Eq. (1) are expected to be massive.[5]] The $k=1$ model is equivalent to a free massless boson[6] and so the $s=\frac{1}{2}$ system is in the same universality class as the classical xy model (and many other systems). However, the higher-k models have nontrivial interactions and belong to new universality classes. All critical exponents have been calculated exactly,[7] for all k. In this Letter we show that the zero-temperature, zero-field susceptibility is a universal number (when scaled by v_s) proportional to k. This allows a direct experimental test of the critical theory.

We begin with $s=\frac{1}{2}$ and $\Delta=0$, the model solved exactly by Lieb, Schultz, and Mattis.[8] It is mapped, via the Jordan-Wigner transformation

$$S_n^- = \exp\left[i\pi \sum_{m=1}^{n-1} \psi_m^\dagger \psi_m \right] \psi_n, \quad S_n^z = \psi_n^\dagger \psi_n - \tfrac{1}{2}, \quad (2)$$

onto a free-fermion system:

$$H=\tfrac{1}{2}\sum_i (\psi_i^\dagger \psi_{i+1} + \psi_{i+1}^\dagger \psi_i) = -\sum_q \psi_q^\dagger \psi_q \cos q, \quad (3)$$

where

$$\psi_n = (-1)^n \sum_q \exp[iqn]\psi_q/\sqrt{N}, \quad (4)$$

$$q=2\pi n/N \quad (n=0,1,2,\ldots,N-1).$$

The total z spin becomes

$$\mathcal{S}^z = \sum_i (\psi_i^\dagger \psi_i - \tfrac{1}{2}) = \sum_q (n_q - \tfrac{1}{2}), \quad (5)$$

where $n_q = \psi_q^\dagger \psi_q$ is the occupation number (0 or 1) of the momentum-q state. The zero-field susceptibility is[9]

$$\chi = \langle (\mathcal{S}^z)^2 \rangle / TN$$
$$= (1/4TN) \sum_q \mathrm{sech}^2[\cos(q/2T)]. \quad (6)$$

As $T\to 0$ the sum is dominated by $q\approx \pm\pi/2$, the two branches of the Fermi surface, giving

$$\chi \to (1/2T)\int_{-\infty}^{\infty} (dq/2\pi)\mathrm{sech}^2(q/2T) = 1/\pi. \quad (7)$$

Since the Fermi velocity is $v_s = -(d/dq)\cos q|_{\pi/2} = 1$, we may write $\chi = (1/\pi)v_s$ (at $T=0$). It is instructive to derive this $T=0$ result another way. Since only $q\approx \pm\pi/2$ contribute we may write

$$\psi(n) = i^n \psi_L(n) + (-i)^n \psi_R(n), \quad (8)$$

where ψ_L and ψ_R are slowly varying. H becomes a relativistic free-fermion Hamiltonian and we may write

$$\mathcal{S}^z = \int dx :\psi_L^\dagger \psi_L + \psi_R^\dagger \psi_R: = \int dx\, J_0(x), \quad (9)$$

where the colons denote normal ordering in the relativistic free-fermion vacuum. J_0 is the relativistic fermion number density. This can be bosonized[10] by use of $J_\mu = \epsilon_{\mu\nu}\partial^\nu \phi/\sqrt{\pi}$, where ϕ is a conventionally normalized massless free boson. The normalization in this equation can be fixed by the current commutator

$$[J_\mu(x), J_\nu(y)] = \epsilon_{\mu\nu}\delta'(x-y)/\pi. \quad (10)$$

Finally χ can be calculated with use of the finite-temperature boson propagator:

$$\chi = \frac{1}{\pi T}\lim_{q\to 0} q^2 T \sum_{n=-\infty}^{\infty} [q^2 + (2n\pi T)^2]^{-1} = \frac{1}{\pi}. \quad (11)$$

Now consider arbitrary $\Delta \leq 1$. The critical theory is expected to remain a free boson.[1] Working always with a conventionally normalized boson we may write $J_\mu = \gamma \epsilon_{\mu\nu} \partial^\nu \phi$ (setting the velocity of light equal to 1). The problem is to find $\gamma(\Delta)$. We do this by observing that[1] $\sum_i S_i^- S_{i+1}^- = -2i\int dx\, \psi_L \psi_R$. The bosonized form is[1] $\psi_L \psi_R \sim \exp[i\beta(\phi_L - \phi_R)]$, where ϕ_L and ϕ_R are left- and right-moving parts of $\phi = \phi_L + \phi_R$. $\beta(\Delta)$ is known exactly from the Bethe *Ansatz*[1,11]: $\beta^2 = 8\cos^{-1}(-\Delta)$. γ can then be fixed by the demand that the commutator

$$[\textstyle\sum_i S_i^z, \sum_i S_i^- S_{i+1}^-] = -2\sum_i S_i^- S_{i+1}^- \qquad (12)$$

be correctly reproduced. Since

$$[\partial_1\phi(x), \exp\{i\beta(\phi_L - \phi_R)\}] = \beta\delta(x-y)\exp[i\beta(\phi_L - \phi_R)], \qquad (13)$$

we conclude that $J_0 = (2/\beta)\partial_1\phi$, and thus $v_s \chi = 4/\beta^2 = 1/2\cos^{-1}(-\Delta)$. The spin-wave velocity v_s is not known exactly, as a function of Δ; it appears in χ in a way determined by dimensional analysis. Note that $v_s\chi(\Delta=1) = 1/2\pi = \frac{1}{2}v_s\chi(\Delta=0)$.

We now reconsider the isotopic $s=\frac{1}{2}$ model ($\Delta=1$). A different fermionization[2,12] which manifestly preserves the SU(2) symmetry is useful in this case: $\mathbf{S} = \frac{1}{2}\psi^{\dagger\alpha}\sigma_\alpha{}^\beta\psi_\beta$. The fermions now carry a spin index and the constraint $\psi^\dagger\psi = 1$ (one particle per site) must be enforced. Since the band is half filled we again introduce left- and right-moving fermions as in Eq. (8):

$$\mathscr{S}^z = \tfrac{1}{2}\int dx[\psi_L^\dagger \sigma^z \psi_L + \psi_R^\dagger \sigma^z \psi_R]. \qquad (14)$$

If we treated the fermions as being noninteracting we would obtain a value of χ one-half as big as for $\Delta=0$ (as a result of the two explicit factors of $\frac{1}{2}$ and the single sum over spins), $\chi = 1/2\pi v_s$. (This value was obtained above.) In fact the fermions *are* interacting in this case. The critical theory is derived by introduction of separate bosons for charge and spin. The charge boson is massive and can be eliminated leaving either a massless free spin boson,[12] or equivalently a $k=1$ WZW σ model.[2] However, the only thing that matters for our purposes is that the current two-point function at low momentum is unaffected by the interactions. The reason is that this two-point function is uniquely fixed by current conservation and conformal invariance up to an overall constant. The constant is proportional to the central charge, k, of the (Kac-Moody) current algebra:

$$[J^a(x_-), J^b(y_-)] = i\epsilon^{abc}J^c(x_-)\delta(x_- - y_-) + (ik/4\pi)\delta^{ab}\delta'(x_- - y_-). \qquad (15)$$

(Here J^a are left currents and $x_- = x_0 - x_1$.) k is only permitted to take on integer values (the Kac-Moody algebra only has unitary representations for k integer). Thus k cannot get renormalized in any continuous fashion (this property can also be derived[4] by topological arguments in the WZW models) and so retains the value $k=1$ which it has for the free-fermion current of Eq. (14).

This approach easily generalizes[2] to higher spin isotropic systems. To obtain spin s we introduce $2s$ "colors" as well as 2 spins, $\psi_{i\alpha}$ ($\alpha = 1,2$; $i = 1, 2, \ldots, 2s$) and write $\mathbf{S} = \frac{1}{2}\psi^{\dagger i\alpha}\sigma_\alpha{}^\beta\psi_{i\beta}$ with the constraint $\psi^{\dagger i\alpha}\psi_{j\alpha} = \delta_j^i$ ($2s$ particles per site in a color singlet state). Again the band is half filled and so we introduce ψ_L and ψ_R as before:

$$\mathscr{S}^z = \tfrac{1}{2}\int dx[\psi_L^{\dagger i}\sigma^z\psi_{Li} + \psi_R^{\dagger i}\sigma^z\psi_{Ri}]. \qquad (16)$$

Treating the fermions as free gives a value of χ which is $2s$ times as big as for spin $\frac{1}{2}$, because of the sum over $2s$ colors: $\chi = s/\pi v_s$. In fact, the fermions are not free. The critical theory is derived[2] by introduction of separate bosons for charge, color, and spin. The charge and color bosons are massive and decouple, leaving only the spin bosons which comprise the $k=2s$ WZW σ model. The essential point is that the free-fermion current algebra is not modified by this decoupling (i.e., the central charge, $k=2s$, is not renormalized).

We now compare with other results. The spin-s isotropic antiferromagnet is Bethe-*Ansatz* integrable[13] for a special choice of nonquadratic Hamiltonian:

$$H_s = \sum_{l=1}^{2s}\sum_{k=1}^{l}\frac{1}{k}\sum_i P_l(\mathbf{S}_i\cdot\mathbf{S}_{i+1}), \qquad (17)$$

where P_l is the projection operator onto spin l for a pair of neighboring sites. (This can be written as a $2s$-order polynomial in $\mathbf{S}_i\cdot\mathbf{S}_{i+1}$.) For these models[14] $v_s = \pi/2$ and $\chi = 2s/\pi^2$, in agreement with the present result, which we expect to be universal by the above arguments. Apparently, modifying the integrable Hamiltonian produces a mass gap in the s-integer case.[2,5] In the half-integer case we expect the mass gap to remain zero and χv_s to remain constant for a wide range of Hamiltonians, including the realistic quadratic one.[15] This is so because k cannot vary continuously and it seems rather unlikely that it would make integer jumps as H is varied. However, the latter may not be completely impossible and it might seem natural that all quadratic half-integer-s models are in the free-boson ($k=1$) universality class. In this case, one has $\chi v_s = 1/2\pi$, independent of s. Thus it is important to compare with other measurements.

In the $s=\frac{1}{2}$ case there is no dispute. The integrable model is quadratic. Exact diagonalization of a finite chain[16] gave a number in excellent agreement with the result $\chi = 1/\pi^2$ ($v_s = \pi/2$).

The classical antiferromagnetic chain was solved by Fisher.[17] Naively, one might expect the classical limit to be good at large s. It will, however, always break down at sufficiently low temperature. This can be understood from the perturbative corrections to linear spin-wave theory. The spin-wave coupling is $O(1/s)$ and so the linear (classical) theory is in general a good approximation. However, this coupling constant is renormalized towards large values at large distances or low energies [exactly as in the O(3) σ model] and so becomes ~ 1 at a temperature[5,18] $T \sim \exp\{-\pi[s(s+1)]^{1/2}\}$. It seems reasonable to expect the spin-wave velocity of the linear theory, $v_s = 2s$, to become exact at large s since the effects which renormalize the coupling can be described by a relativistic theory (in which the speed of "light" is not renormalized because of Lorentz invariance). The classical susceptibility is[17]

$$\chi(T) = \frac{s(s+1)}{3T} \frac{1-\coth[s(s+1)/T] + T/s(s+1)}{1+\coth[s(s+1)/T] - T/s(s+1)} \underset{T\to 0}{\to} \frac{1}{6}; \tag{18}$$

combining the classical susceptibility with the linear spin-wave velocity gives $\chi v_s = s/3$. Remarkably, this differs from the exact quantum result by only a factor of $\pi/3 \approx 1.05$. Thus, for large spin, we expect $\chi(T)$ to be given approximately by the classical result [Eq. (18)] down to some very small temperature at which a small ($\sim 5\%$) but rapid crossover to quantum behavior occurs. Note that if the higher-spin systems remained in the free-boson universality class an enormous jump in χ (to essentially zero) would have to occur at low T.

We now turn to experimental data. $CuCl_2 \cdot 2NC_5H_5$ is a nearly isotropic, one-dimensional, spin-$\frac{1}{2}$ antiferromagnet [with a coupling J multiplying the Hamiltonian of Eq. (1) of 26.8 K] down to about 2 K where three-dimensional effects take over. The spin-wave spectrum[19] agrees well with the theoretical prediction[20] $E(q) = (\pi/2)J|\sin q|$ and gives $v_s = \pi J/2$. The susceptibility[21] (Fig. 1) is in excellent agreement, over a large range of T, with the result from exact diagonalization of a finite chain.[16] Hence extrapolation to $T=0$ gives good agreement with the exact theoretical value, $\chi v_s = 1/2\pi$. $(CH_3)_4NMnCl_3$ is a nearly isotropic [$\Delta = 0.99$ in Eq. (1)] one-dimensional spin-$\frac{5}{2}$ antiferromagnet (with $J = 13.2$ K) down to about 1 K. The spin-wave spectrum[22] is again linear near 0, giving $v_s = 70.7$ K. Parallel and perpendicular susceptibilities[23] are shown in Fig. 2. They can be well fitted over a large temperature range by the classical theory with $J = 13.2$ K and $\Delta = 0.99$. [Classically,[23] a large deviation between $\chi_\parallel$ and $\chi_\perp$ occurs for $T \leq s(s+1)J\sqrt{\Delta}$ with $\chi_\parallel$ and $\chi_\perp$, respectively, $\frac{3}{2}$ and $\frac{3}{4}$ times the isotropic value at $T, \Delta \to 0$.] Using this value of J we find that v_s is only 7% larger than the linear spin-wave prediction of $2sJ$. Large deviations from the classical theory are seen below 20 K, suggesting the onset of quantum effects. The predicted value of $\chi(0)$ for the isotropic case, $s/\pi v_s = 0.017$ cm^3/mol, is also shown in Fig. 2. We expect $\chi_\parallel$ (at $T=0$) to increase smoothly with anisotropy as $(1-\Delta)^{1/2}$, as in the $s=\frac{1}{2}$ case discussed above. Thus agreement between theory and experiment is good. On the other hand, assuming the free boson ($k=1$) critical theory leads to $\chi = 1/2\pi v_s = 0.0034$ cm^3/mol. (This is not shown in Fig. 2 because it is off scale.) This value is probably ruled out unless one can argue that the true one-

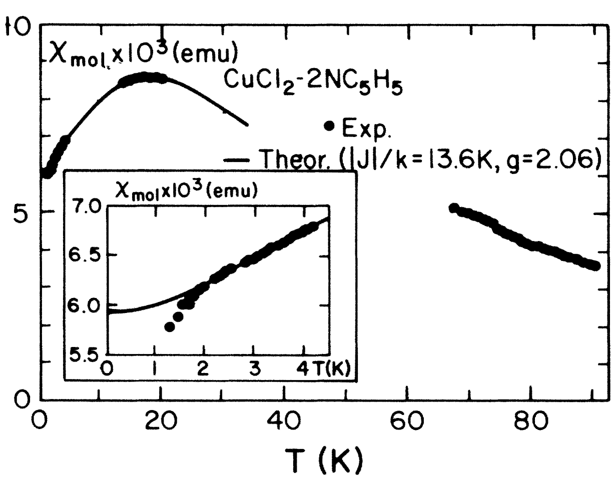

FIG. 1. Susceptibility of $CuCl_2 \cdot 2NC_5H_5$ from Ref. 21. The solid line is the result from exact diagonalization of a finite chain (Ref. 16). It agrees with the exact theoretical prediction at $T=0$.

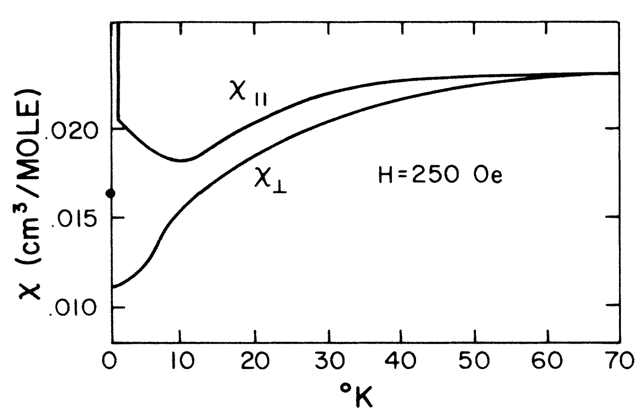

FIG. 2. Susceptibility of $(CH_3)_4NMnCl_3$ from Ref. 23. The theoretical prediction for χ at $T=0$ and vanishing anisotropy ($\chi = 0.017$ cm^3/mol) is marked.

dimensional χ drops dramatically to this value at $T \lesssim 1°$ and this is wiped out by three-dimensional effects. The close agreement between quantum and classical theories, noted above, makes it difficult to judge whether the attainable temperature (about 1 K) is in the quantum regime. It may be possible to resolve this issue by a more complete comparison of theory and experiment.[24]

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