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LETTER TO THE EDITOR

# Thermodynamic properties of the Haldane spin chain: a statistical model for the elementary excitations

L-P Regnault†, I A Zaliznyak†‡ and S V Meshkov§

† Laboratoire de Magnetisme et Diffraction Neutronique, Departement de Recherche Fondamentale, Centre d'Etudes Nucléaires de Grenoble, 85X, 38041 Grenoble Cédex, France
‡ Kapitza Institute for Physical Problems, Ulitsa Kosygina 2, 117334 Moscow, Russia
§ Centre des Recherches sur les Tres Basses Temperatures, CNRS, 38042 Grenoble Cédex, France

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**Abstract.** The low-temperature behaviour of the thermodynamic quantities in the one-dimensional 1D antiferromagnet with a Haldane ground state was analysed using a concept of non-interacting quasiparticles as a starting point. The proposed description appeared to be in good agreement with the results of the Monte Carlo study of a 128-site spin chain and experimental data obtained in NENP ($Ni(C_2H_8N_2)_2NO_2ClO_4$) provided that the elementary excitations constituting the Haldane triplet obey Fermi statistics.

The problem of finding an exact quantum-mechanical solution for the ground state (GS) and elementary excitations from it for a nearly isotropic Heisenberg antiferromagnet has always been one of the key points in magnetism. Unfortunately, an explicit analytical solution is obtained only for a few particular Hamiltonians. However, starting from the semiclassical approach, one obtains an ingenious and powerful tool—the spin-wave theory. This gives a consistent description of the spin system in terms of series in $1/S$ as long as the latter converge. This is usually the case for a three-dimensional lattice, but at lower dimension divergencies of the terms accounting for the zero-point spin motion appear in the series, implying non-validity of the N'eel GS. In the seemingly simple but most essential case of the one-dimensional 1D antiferromagnet the breakthrough arrived ten years ago with the works of Haldane [1]. Considering a weakly anisotropic Heisenberg Hamiltonian

$$\mathcal{H} = J\sum_i \{S_i \cdot S_{i+1} + \lambda S_i^z S_{i+1}^z\} + D\sum_i (S_i^z)^2 \tag{1}$$

in the long-wavelength semiclassical ($S \gg 1$) limit he found it to be equivalent to the O(3) non-linear $\sigma$ model (which is known to be renormalizable in the quantum limit) provided the appropriate representation. The mapping established in this way, or more exactly, the result of the renormalization of the corresponding $\sigma$ model, appeared to be crucially dependent on the parity of the spin value $S$ in the chain. The most striking result was found in the case of integer $S$: in a finite range of the anisotropies the GS appears to be non-degenerate with no static and an exponential decay of dynamic correlations, $\langle S_0^\alpha(0) S_n^\alpha(t)\rangle \sim [(-1)^n/|n|^{1/2}]e^{-\kappa|n|}$. The collective modes, initially Goldstone bosons, acquire a dynamically generated gap $\Delta_H \sim e^{-\pi S}$ at $q = \pi$.

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The work of Haldane stimulated a number of studies aimed at obtaining further insight into the new physics discovered in the 1D antiferromagnetic chain of integer spins. It is also the subject of the present paper. One distinguishes three general trends of study: analytical description of the energy spectrum of the Hamiltonian (1) and its field dependences by the virtue of mapping on the solvable field-theoretical models [2, 3], experiments on the $Ni(C_2H_8N_2)_2NO_2ClO_4$ (NENP) crystal, the magnetic system of which was proved to consist of almost non-interacting chains of $Ni^{2+}$ ($S = 1$) spins coupled with the antiferromagnetic in-chain exchange [4, 5], and numerical simulations on finite chains [6–8]. The aim of the present work is not to continue in one of these directions but to calculate the free energy and other thermodynamic quantities for the Haldane $S = 1$ spin chain, relying upon the existent knowledge on its energy spectrum [3–8]. Comparison of their temperature dependences with the results of the new Monte Carlo simulations and measurements in NENP would then suggest a choice of the statistics of the excitations involved in the Haldane triplet.

Thus we consider a spin chain with the Hamiltonian (1), $S = 1$, $\lambda = 0$ and $D \ll J$. Making the numerical estimates we will use the values $J = 46$ K and $D = 0.16$ J found in NENP [4, 5] (neglecting the weak orthorhombic anisotropy). In fact, it is a rather arbitrary choice in the $D/J$ region that corresponds to the Haldane phase [7]. To proceed we will use a phenomenological description of the spectrum, not meeting the challenge to develop an analytical approach to its diagonalization.

It is convenient to start from the isotropic Heisenberg Hamiltonian as a zero approximation and treat the anisotropy perturbatively, as suggested by Affleck [2]. So in zeroth order the total spin $S_{tot}$ and its component $S^z_{tot}$ are conserved. The essential assumption to make here is that together with the wavevector $q$ they constitute a full set of good quantum numbers to classify the energy eigenstates. This, in particular, means that we will use the concept of non-interacting quasiparticles to describe the excited states of the system. Thus, following Haldane, we have the classification: $|\mathrm{GS}\rangle = |S_{tot} = 0, q = 0\rangle = |0\rangle$—the only non-degenerate $S_{tot}$ eigenstate; $|\text{one-particle excited state}\rangle = |S_{tot} = 1, S^z_{tot} = \alpha, q\rangle = |\alpha, q\rangle$—degenerate at all $q$ in $\alpha = 0, \pm 1$; etc. The triplet is separated from the GS by the energy gap $\varepsilon(q) = E_{\alpha,q} - E_{GS}$, $\min\{\varepsilon(q)\} = \varepsilon(\pi) = \Delta_H$.

The perturbation $\mathcal{V}_A = D\sum_i (S^z_i)^2$ commutes with $S^z_{tot}$ leaving it (but not $S_{tot}$) the integral of the motion. In the first order it leads to three principal consequences:

(i) shift of the GS energy $E$:

$$\Delta E^{(1)}_{GS} = \langle 0|\mathcal{V}_A|0\rangle = \frac{1}{3}\sum_\gamma \langle 0|D\sum_i (S^\gamma_i)^2|0\rangle = N\frac{D}{3}S(S+1) \tag{2}$$

(ii) change of the GS by admixing to it $S^z_{tot} = 0$ components of the triplet and states with larger $S$:

$$|\mathrm{GS}\rangle^{(V)} = |0\rangle + \sum_q |0, q\rangle \frac{\langle 0, q|\mathcal{V}_A|0\rangle}{\varepsilon^{(0)}(q)} + \sum |S_{tot} > 1\rangle \tag{3}$$

making use of $\langle \pm 1, q|\mathcal{V}_A|0\rangle = \pm\langle 1, q|[\mathcal{V}_A, S^z_{tot}]|0\rangle = 0$;

(iii) lifting of the triplet degeneracy at each $q$:

$$\begin{aligned} \Delta E^{(1)}_{0,q} &= \langle 0, q|\mathcal{V}_A|0, q\rangle = \delta_0(q) \\ \Delta E^{(1)}_{\pm 1,q} &= \langle \pm 1, q|\mathcal{V}_A| \pm 1, q\rangle = \delta_\pm(q) \end{aligned} \tag{4}$$

(again using the commutation of $V_A$ with $S_{tot}$ and with the $\mathcal{I}^z$ operator of $z$-axis inversion to show $\delta_+(q) = \delta_-(q) = \delta_\pm(q)$).

It should be mentioned that the average shift of the excited triplet is

$$\frac{1}{3}(\Delta E^{(1)}_{0,q} + 2\Delta E^{(1)}_{\pm,q}) = \frac{1}{3}\sum_\gamma\left(\frac{1}{3}Sp\langle\alpha', q|D\sum_i(S_i^\gamma)^2|\alpha, q\rangle\right) = N\frac{D}{3}S(S+1) \tag{5}$$

equal to $\Delta E^{(1)}_{GS}$, so the total energy-level picture acquires a macroscopic shift (2), (5). The gaps of the split triplet then satisfy

$$\begin{aligned}&\frac{1}{3}\sum_\alpha \varepsilon^{(1)}_\alpha(q) = \varepsilon^{(0)}(q) = \varepsilon(q)\\ &\frac{1}{3}(\Delta_0 + 2\Delta_\pm) = \Delta_H.\end{aligned} \tag{6}$$

Not going into the higher orders of perturbation, hereafter we will omit the upper index in $\varepsilon^{(1)}_\alpha(q)$.

In support of the picture developed above we refer to the Monte Carlo (MC) simulations and inelastic neutron scattering (INS) studies in NENP. Both of these confirm the Haldane claim for a singlet ground state and reveal three well defined branches of magnetic excitations. They are seen as the sharp peaks in the spectral function $S^\alpha(q,\omega)$ (Fourier-transformed spin–spin correlator) in the broad neighbourhood of the antiferromagnetic point $q = \pi$ where they exhibit magnon-like dispersion

$$\begin{aligned}&\varepsilon_\alpha(q) = \sqrt{\Delta_\alpha^2 + C^2\sin^2 q^*}\\ &C \simeq 1.9J\sqrt{S(S+1)}\\ &q^* = \pi - q.\end{aligned} \tag{7}$$

The Haldane gap equal to $\Delta_H$ is split by the anisotropy $D/J = 0.16$ into $\Delta_0 = 0.62$ J and $\Delta_\pm = 0.31$ J (figure 1). However, as the point $q = 0$ is approached, peaks broaden and weaken, becoming undetectable by INS for $q \leqslant 0.3\pi$ [5]. MC simulations [7] seem to support the treatment of the excitations at $q \simeq 0$ as being composed of pairs of counterpropagating quasiparticles with $q \simeq \pi$ giving rise to the continuum of energies in the spectrum. This multiparticle continuum is therefore separated from the ground state by the gap $\varepsilon_G(0) = 2\min\{\Delta_\alpha\}$. Generally speaking, it clearly manifests the failure of the above description in terms of the quantum numbers $S_{tot} = 1$, $S^z_{tot} = \alpha$ and $q$. Hence, it cannot be applied to the system in the whole range of energies. In fact, it is the usual situation in condensed-matter physics when only a weakly excited state of the system can be treated in terms of well defined quasiparticles. This simply limits the validity of such treatment to the low-temperature region where the 'wrong' states are not excited.

Now the point is to evaluate the statistical sum $\mathcal{Z} = Sp\{\exp(-\mathcal{H}/T)\} = \exp(-F_m/T)$ over the three bands of non-interacting quasiparticles (7). Doing this we can restrict the summation to the energies $\varepsilon < \varepsilon_G(0)$ implying the results to be valid at $T \leqslant \Delta_\pm$. Actually, this is a routine procedure relevant to that used by Landau to calculate the thermodynamic quantities in the superfluid $He^4$. The difference is that in our case we do not posses *ab initio*

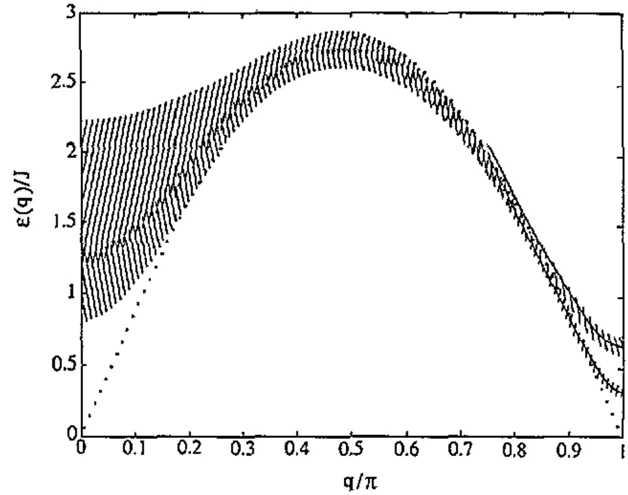


**Figure 1.** Spectral density of the excited states $\rho_q^\alpha(\varepsilon)$ measured in a Monte Carlo numerical experiment for a 128-site closed chain at $T = J/16$. The hatched region corresponds to the effective width of the observed $\rho_q^\alpha(\varepsilon)$ peaks. Solid lines are drawn using (7). Dots are the $\sin q$ law.

knowledge on the statistics of the excitations†. The result for the temperature-dependent part of the free energy is well known

$$F_{\mathrm{m}} = \mp T \sum_\alpha \sum_q \ln\{1 \pm \exp[-\varepsilon_\alpha(q)/T]\} \tag{8}$$

where we retain the upper sign for the case of the fermion quasiparticles and the lower one for the bosons. Hereafter using the basic relations of thermodynamics one easily obtains the magnetization $M = -\partial F_{\mathrm{m}}/\partial H$ ($H$ is the external magnetic field to be included in the Hamiltonian) and the magnetic specific heat $C_{\mathrm{m}} = -\partial^2 F_{\mathrm{m}}/\partial T^2$. Transforming the sum into the integral one has for the latter (per spin)

$$C_{\mathrm{m}} = \sum_\alpha \int \frac{\varepsilon_\alpha^2(q)}{T^2} \frac{\exp[-\varepsilon_\alpha(q)/T]}{1 \pm \exp[-\varepsilon_\alpha(q)/T]}\, \mathrm{d}q. \tag{9}$$

Due to the above restriction in energy one can limit the integration to the close vicinity of the 1D Brillouin-zone centre $|q^*| \leqslant 0.1\pi$. In the limit $T \ll \Delta_\alpha$ the Boltzman statistics is naturally recovered. Making the appropriate expansions we easily obtain the analytical estimates for the integrals (8), (9)

$$\left.\begin{array}{l} F_{\mathrm{m}} \simeq -(T/C)\sum_\alpha \sqrt{2\pi T \Delta_\alpha}\exp(-\Delta_\alpha/T) \\ \\ C_{\mathrm{m}} \simeq -(1/C)\sum_\alpha \sqrt{2\pi T \Delta_\alpha}(\Delta_\alpha^2/T^2)(1 + T/\Delta_\alpha)\exp(-\Delta_\alpha/T) \end{array}\right\} \quad T/\Delta_\alpha \ll 1. \tag{10}$$

Being at the moment unable to extract $C_{\mathrm{m}}$ from the MC simulations we can compare the obtained results only with the experimental data available [9]. Unfortunately, due to the unknown lattice contribution the latter have been accurately defined only at low

† For instance, in the continuum limit Hamiltonian (1) can be mapped either on the bosonic or fermionic field [2, 3]. In any case, in one dimension at $T = 0$ the question of the statistics is merely a matter of choice of the variables and convenience of the treatment.

temperatures. As is shown by figure 2, in this region numerical integration of (9) gives the same results for both statistical models. At $T \leqslant 0.1J$ they are also well reproduced by the expression (10). At higher temperature curve (10) goes below the Fermi one (instead of being in between it and the Bose one) due to the failure of the expansions used to obtain it from the Boltzman limit of (9).

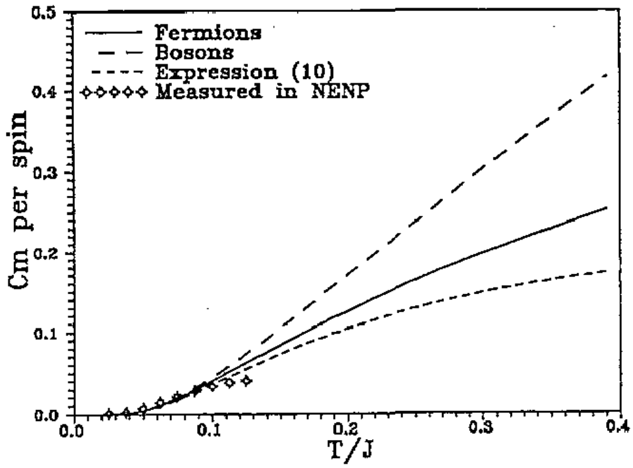


**Figure 2.** Magnetic heat capacity calculated with (9), (10) and measured in NENP. Experimental points are taken from [9].

It is more interesting to proceed with the susceptibility: for this we can compare our description with the MC results and measurements in NENP up to $T \sim \Delta_\pm$ where the difference between the predictions of different statistical models is quite pronounced. At this point we need to introduce the field dependences in the excitation spectra. These are caused by the addition of the term $\mathcal{V}_Z = \boldsymbol{H} \sum_i \boldsymbol{S}_i$ to the Hamiltonian. In fact, if the field is applied along the $z$ axis it is quite simple: since we associate the quasiparticles with the eigenstates of $S^z_{\mathrm{tot}}$, the magnetic field will simply introduce the Zeeman splitting $\varepsilon_\pm(q, H) = \varepsilon_\pm(q) \pm H$, $\varepsilon_0(q, H) = \varepsilon_0(q)$. As was also pointed out by Affleck [2] this result is exact in the framework of the description adopted. Introducing these field dependences into (8) and taking the derivatives we obtain the susceptibility (per spin)

$$\chi^z = \frac{2}{T} \int \frac{\exp[-\varepsilon_\pm(q)/T]}{\{1 \pm \exp[-\varepsilon_\pm(q)/T]\}^2} \, \mathrm{d}q. \tag{11}$$

In the Boltzman limit we obtain the same estimate $\chi^z \simeq (2/C)\sqrt{2\pi T \Delta_\pm} \exp(-\Delta_\pm/T)$ as reported in [2] (correcting minor arithmetical errors made there).

If the field is along, say, the $x$ axis, the total perturbation $\mathcal{V} = \mathcal{V}_A + \mathcal{V}_Z$ is no longer diagonal in the $S^z_{\mathrm{tot}}$ representation and the degeneracy of the triplet is lifted completely. Working out the first-order corrections (given by the eigenvalues of the $3 \times 3$ matrix $\langle \alpha', q | D \sum_i (S^z_i)^2 - H S^x_{\mathrm{tot}} | \alpha, q \rangle$) and using (4)–(6) we have for the two gaps

$$\varepsilon_{0,\pm}(q, H) = \frac{\varepsilon_0(q) + \varepsilon_\pm(q)}{2} \mp \sqrt{\left(\frac{\varepsilon_0(q) - \varepsilon_\pm(q)}{2}\right)^2 + H^2}. \tag{12}$$

The third gap equal to $\varepsilon_\pm(q)$ is field independent. In the long-wavelength limit these expressions coincide with those derived by Tzvelick [3] up to the terms $\sim \mathrm{O}[(q^*)^4] +$

$O[(q^*)^2(\Delta_0 - \Delta_\pm)^2/\Delta_H^2]$. At $q^* = 0$ the coincidence is exact (this is easily seen after the multipication of (12) by itself). Thus the field dependences $\Delta_\alpha(H)$ given by (12) are in a surprisingly good agreement with those obtained in MC [8] and INS [4] experiments even extrapolated to high fields (the critical field $H_c = \sqrt{\Delta_0\Delta_\pm}$ is a natural limit of the validity of the perturbative treatment). Using the above field dependences one obtains for $\chi^{x,y}$

$$\chi^{x,y} = \frac{2}{T}\int\left[\frac{\exp[-\varepsilon_\pm(q)/T]}{1\pm\exp[-\varepsilon_\pm(q)/T]} - \frac{\exp[-\varepsilon_0(q)/T]}{1\pm\exp[-\varepsilon_0(q)/T]}\right] \times \frac{dq}{\exp[-\varepsilon_0(q)/T] - \exp[-\varepsilon_\pm(q)/T]} \tag{13}$$

which coincides with (11) in the isotropic ($\Delta_0 \to \Delta_\pm$) limit.

To check whether the description within the concept of non-interacting quasiparticles (7), (8) is relevant to our system (1), a numerical experiment using the world-line MC approach was performed (for a detailed description see [7]). This allows us to study a chain of 128 spins that is much longer than the correlation length in the Haldane state. The static susceptibility was extracted at $T/J = \frac{1}{4}, \frac{1}{5}, \frac{1}{8}$ and $\frac{1}{16}$. The error bars of the 'measurement' were estimated to be less than $5\times10^{-3}$ (in the scale of figure 3(*a*)). This gives a relative inaccuracy of less than 5%. An exception is the value at $T = J/16$ where this inaccuracy is almost five times higher.

In figure 3(*a*) we present the MC points for $\chi$ together with the results of the numerical integration of expressions (11), (13). We obtain an excellent agreement of our description with the MC experiment assuming that the elementary excitations are fermions. This conclusion receives further confirmation when we compare our results with the molar susceptibility measured in NENP, figure 3(*b*) (we have to multiply the values calculated with (11), (13) by $N_A(g_\alpha\mu_B)^2$, where $N_A$ is Avogadro's number, $\mu_B$ Bohr's magneton and $g_\alpha$ the $g$ factor corresponding to the field direction). Principal is the excellent coincidence of the results given by the model with non-interacting fermions for $\chi^z$ with those of MC and direct measurements in $Ni(C_2H_8N_2)_2NO_2ClO_4$ in the whole region of the validity of the description used, $T \leqslant \Delta_\pm$. The minor discrepancy between the calculated and measured $\chi^{x,y}$ mainly originates from the temperature-independent part of the free energy that was omitted in (8). This corresponds to the GS susceptibility caused by the anisotropy $D$. In the perturbative treatment it arises from the fourth-order correction to the GS energy

$$\Delta E_{GS}^{(4)} = H^2\sum_q \frac{|\langle 0|V_A|0,q\rangle|^2}{\varepsilon^3(q)} \sim H^2\frac{D^2}{\Delta_H^3}$$
$$\chi^{x,y}(0) \sim \frac{D^2}{\Delta_H^3} \simeq 2\chi^{cl}\left(\frac{D}{J}\right)^2 \tag{14}$$

(here $\chi^{cl} = (4JS)^{-1}$, in NENP $\chi^{cl} \simeq 9.1\times10^{-3}$ CGS mol$^{-1}$). The coefficient 2 in the last approximate equality arises from the comparison of (14) with the experimental value $\chi^{x,y}(T = 0) \simeq 5\times10^{-3}$ CGS mol$^{-1}$ measured in NENP. This temperature-independent contribution (14) should be added to $\chi^{x,y}$ from (13).

In conclusion, the problem of the statistics of the excitations, being simply a matter of choice of the variables at $T = 0$ in 1D, acquires physical importance as one tries to extend the description to higher temperatures. Thus we show that the low-temperature properties of the 1D Heisenberg antiferromagnet (1) found in MC experiment and measured

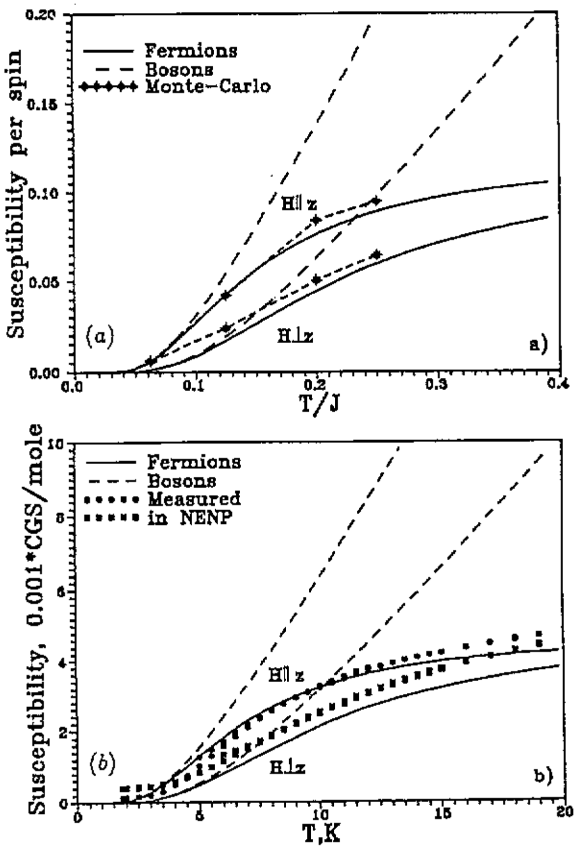


**Figure 3.** (*a*) Susceptibility per spin calculated with our model for both statistics together with that extracted from MC experiment. (*b*) Comparison of the same calculation for the molar susceptibility with our measurements in NENP for $H \| z$ and $H$ in an arbitrary direction perpendicular to $z$.

in NENP can be described in terms of the elementary excitations (7) constituting the non-interacting Fermi gas of quasiparticles. This does not exclude the possibility that a theory including the Bose excitations can be developed, but implies that in such a theory the strong interparticle interaction has to be considered. Our conclusion gives further support to analytical approaches involving the fermionization of the Hamiltonian (1). In addition, such treatment can provide a plausible physical picture for the Haldane ground state and fermionic excitations from it as a spin-zero defect [10].

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