The magnetocaloric effect in integrable spin-\(s\) chains

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Abstract. We study the magnetocaloric effect for the integrable antiferromagnetic high spin chain. We present an exact computation of the Grüneisen parameter, which is closely related to the magnetocaloric effect, for the quantum spin-\(s\) chain in the thermodynamical limit by means of Bethe ansatz techniques and the quantum transfer matrix approach. We have also calculated the entropy \(S\) and the isentropes in the \((H, T)\) plane. We have been able to identify the quantum critical points \(H_c^{(s)} = 2/(s + 1/2)\) looking at the isentropes and/or the characteristic behaviour of the Grüneisen parameter.

Keywords: quantum integrability (Bethe ansatz), thermodynamic Bethe ansatz, spin chains, ladders and planes (theory), quantum phase transitions (theory)
1. Introduction

The magnetocaloric effect has been known of for more than a hundred years [1] and it is related to the temperature change of magnetic systems induced by an adiabatic variation of the external magnetic field. In recent years it has received considerable attention in view of new potential cooling applications [2].

Many different families of magnetic materials ranging from ferromagnetic and ferrimagnetic to antiferromagnetic systems have been shown to present large or unusual magnetocaloric effects [3]. In particular, the magnetocaloric effect has been measured in (quasi-)one-dimensional materials which behave as quantum spin-1/2 chains [4] and high spin chains [5].

Moreover the existence of the magnetocaloric effect in one-dimensional systems has been studied theoretically for the spin-1/2 Heisenberg chain [6], for the spin-s chain [7] and for mixed-spin chains [8] by means of numerical calculations. There are also some exact results for the XY chain in a transverse field [6] and for the Ising model [6,9]. Recently the magnetocaloric effect and the isentropes in the magnetic field/temperature \((H,T)\) plane have been obtained exactly by Bethe ansatz techniques for the integrable spin-1/2 Heisenberg chain [10].

The magnetocaloric effect \(\partial T/\partial H\) and the related quantity called the Grüneisen parameter \(\Gamma_H\) have been pointed out as important tools for detecting and classifying quantum critical points [9,11]. The Grüneisen parameter for a magnetic systems can be written as

\[
\Gamma_H = \frac{1}{T} \left( \frac{\partial T}{\partial H} \right)_S = -\frac{1}{C_H} \left( \frac{\partial M}{\partial T} \right)_H,
\]

where \(C_H\) is the specific heat at a constant magnetic field and \(\partial M/\partial T\) is the temperature variation of the magnetization \(M\). This parameter \(\Gamma_H\) has a characteristic sign change close to the quantum critical point, which is due to the accumulation of entropy at the critical point [9].

The integrable spin-s generalization of the Heisenberg model [12] was exactly solved long ago [13], providing all the eigenvalues and eigenvectors in terms of the Bethe equations. Its thermodynamic properties were first studied [13,14] by means of the

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thermodynamic Bethe ansatz (TBA) method \([15]\), which consists of using an infinite number of nonlinear integral equations (NLIE) for the free energy. Alternatively, using the quantum transfer matrix (QTM) approach \([16]\) a finite number of NLIE \([17]\) were derived, which are more suitable for practical calculations.

Here we are interested in the exact computation of the magnetocaloric effect \((\Gamma_H)\), entropy and the isentropes in the \((H,T)\) plane for the integrable antiferromagnetic spin-\(s\) chain. The thermodynamic quantities required to achieve this goal, like entropy, specific heat and magnetization, are determined as a function of temperature and magnetic field by means of the solution of a finite set of NLIE arising from the QTM approach \([17]\).

This paper is organized as follows. In section 2, we outline the integrable Hamiltonians and the associated integral equations. In section 3, we present our results for the magnetocaloric effect and the isentropes in the \((H,T)\) plane. Our conclusions are given in section 4.

2. Hamiltonian and integral equations

The Hamiltonians of the integrable spin-\(s\) generalization of the Heisenberg model for \(s = 1/2, 1\) and \(3/2\) are given by

\[
\mathcal{H}^{(1/2)} = J \sum_{i=1}^{L} \left[ \frac{1}{4} \vec{S}_i \cdot \vec{S}_{i+1} \right],
\]

\[
\mathcal{H}^{(1)} = \frac{J}{4} \sum_{i=1}^{L} \left[ 3 + \vec{S}_i \cdot \vec{S}_{i+1} - (\vec{S}_i \cdot \vec{S}_{i+1})^2 \right],
\]

\[
\mathcal{H}^{(3/2)} = \frac{J}{30} \sum_{i=1}^{L} \left[ 234 - 27 \vec{S}_i \cdot \vec{S}_{i+1} + 8(\vec{S}_i \cdot \vec{S}_{i+1})^2 + 16(\vec{S}_i \cdot \vec{S}_{i+1})^3 \right],
\]

where \(L\) is the number of sites and \(\vec{S}_i = (\hat{S}_i^x, \hat{S}_i^y, \hat{S}_i^z)\) are the \(SU(2)\) generators.

One can write a closed formula for the Hamiltonian assuming a generic spin-\(s\) value as follows:

\[
\mathcal{H}(s) = \frac{J}{2} \sum_{i=1}^{L} Q_s(\vec{S}_i \cdot \vec{S}_{i+1}) - H \sum_{i=1}^{L} \hat{S}_i^z,
\]

where

\[
Q_s(x) = \sum_{j=0}^{2s} \left[ 2\psi(j+1) - \psi(1) - \psi(2s+1) \right] \prod_{k=0 \atop k \neq j}^{2s} \frac{x - x_k}{x_j - x_k},
\]

with \(x_k = \frac{1}{2} [k(k+1) - 2s(s+1)]\), \(\psi(x)\) the digamma function and \(J\) is the exchange constant. From now on we assume \(J = 1\). Note that we have also added a Zeeman term in the Hamiltonian \((5)\).

The free energy of the system per lattice site calculated at the thermodynamic limit \((L \to \infty)\) is given by

\[
f(T,H) = f_0 - T(K * \ln BB)(0),
\]

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where \( f_0 = \psi(2s + 1) - \psi((2s + 1)/2) + \psi(\tfrac{1}{2}) - \psi(1), \) \( K(x) = \pi/\cosh [\pi x] \) and the symbol \(*\) denotes the convolution \( f * g(x) = \int_{-\infty}^{\infty} f(x-y)g(y) \, dy.\)

The auxiliary functions \( b(x), \overline{b}(x) \) and the simply related functions \( B(x) = b(x) + 1 \) and \( \overline{B}(x) = \overline{b}(x) + 1 \) are solutions of the following set of nonlinear integral equations [17]:

\[
\begin{pmatrix}
\ln y^{(1/2)}(x) \\
\vdots \\
\ln y^{(s-1/2)}(x) \\
\ln b(x) \\
\ln \overline{b}(x)
\end{pmatrix}
= \begin{pmatrix}
0 \\
0 \\
-\beta d(x) + \beta H \\
-\beta d(x) - \beta H
\end{pmatrix} + \mathcal{K} \ast \begin{pmatrix}
\ln Y^{(1/2)}(x) \\
\vdots \\
\ln Y^{(s-1/2)}(x) \\
\ln B(x) \\
\ln \overline{B}(x)
\end{pmatrix}, \tag{8}
\]

where \( d(x) = \pi/(2 \cosh [\pi x]), \) \( \beta = 1/T \) is the inverse of temperature and \( H \) is the magnetic field.

The kernel matrix is given explicitly by

\[
\mathcal{K}(x) = \begin{pmatrix}
0 & K(x) & 0 & \cdots & 0 & 0 & 0 & 0 \\
K(x) & 0 & K(x) & \vdots & \vdots & \vdots & \vdots & \vdots \\
0 & K(x) & 0 & \cdots & 0 & 0 & 0 & 0 \\
\vdots & \vdots & \vdots & \ddots & \ddots & \ddots & \ddots & \ddots \\
0 & 0 & \cdots & 0 & K(x) & 0 & 0 & 0 \\
0 & 0 & \cdots & 0 & 0 & K(x) & F(x) & -F(x + i) \\
0 & 0 & \cdots & 0 & 0 & K(x) & -F(x - i) & F(x)
\end{pmatrix}, \tag{9}
\]

which is a matrix of dimension \((2s+1) \times (2s+1)\) with \( F(x) = \int_{-\infty}^{\infty} e^{-|k|/2+ikx}/(2 \cosh [k/2]) \, dk.\)

In order to obtain the desired thermodynamical quantities, we can calculate the derivatives of the free energy with respect to temperature \( T \) (or more conveniently \( \beta \)) and magnetic field \( H \). It turns out to be more efficient to calculate the derivatives of the free energy in terms of the solutions of linear integral equations. These equations are obtained by differentiation of equation (8). In this way we can avoid numerical differentiation of the free energy.

Specifically one can write the entropy \( S = -(\partial f/\partial T)_H = \beta^2 (\partial f/\partial \beta)_H \) as follows:

\[
S = (K \ast \ln BB)(0) - \beta (K \ast \partial_{\beta} \ln BB)(0), \tag{10}
\]

where \( \partial_{\beta} \ln B(x) = [b(x)/(b(x) + 1)][, \partial_{\beta} \ln \overline{b}(x)] = [\overline{b}(x)/(\overline{b}(x) + 1)][, \partial_{\beta} \ln b(x)] \) and \( \partial_{\beta} \ln Y^{(j)}(x) = [y^{(j)}(x)/(y^{(j)}(x) + 1)][, \partial_{\beta} \ln y^{(j)}(x)] \) for \( j = 1, 2, \ldots, s-1/2 \). These new auxiliary functions should satisfy the following system of linear integral equations:

\[
\begin{pmatrix}
\partial_{\beta} \ln y^{(1/2)}(x) \\
\vdots \\
\partial_{\beta} \ln y^{(s-1/2)}(x) \\
\partial_{\beta} \ln b(x) \\
\partial_{\beta} \ln \overline{b}(x)
\end{pmatrix}
= \begin{pmatrix}
0 \\
0 \\
-d(x) + \tfrac{H}{2} \\
-d(x) - \tfrac{H}{2}
\end{pmatrix} + \mathcal{K} \ast \begin{pmatrix}
\partial_{\beta} \ln Y^{(1/2)}(x) \\
\vdots \\
\partial_{\beta} \ln Y^{(s-1/2)}(x) \\
\partial_{\beta} \ln B(x) \\
\partial_{\beta} \ln \overline{B}(x)
\end{pmatrix}. \tag{11}
\]

To obtain the entropy in the \((H,T)\) plane, one has to solve the above equations (8) and (11), varying the temperature and the magnetic field.

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The specific heat $C_H = T(\partial S/\partial T)_H = -\beta(\partial S/\partial \beta)_H$ can be obtained from (10):

$$C_H = \beta^2(K \ast \partial^2_{\beta} \ln B \bar{B})(0),$$

(12)

which is given in terms of the solution to the following linear integral equations:

$$
\begin{pmatrix}
\partial^2_{\beta} \ln y^{(1/2)}(x) \\
\vdots \\
\partial^2_{\beta} \ln y^{(s-1/2)}(x) \\
\partial_{\beta} \ln b(x) \\
\partial_{\beta} \ln \bar{b}(x)
\end{pmatrix}
= \mathcal{K} \ast 
\begin{pmatrix}
\partial^2_{\beta} \ln Y^{(1/2)}(x) \\
\vdots \\
\partial^2_{\beta} \ln Y^{(s-1/2)}(x) \\
\partial_{\beta} \ln B(x) \\
\partial_{\beta} \ln \bar{B}(x)
\end{pmatrix},
$$

(13)

where \( \partial^2_{\beta} \ln B(x) = [b(x)/(b(x) + 1)]\{[\partial_{\beta} \ln b(x)]^2/(b(x) + 1) + [\partial^2_{\beta} \ln b(x)]\} \) and \( \partial^2_{\beta} \ln Y^{(1)}(x) = [y^{(1)}(x)/(y^{(1)}(x) + 1)]\{[\partial_{\beta} \ln y^{(1)}(x)]^2/(y^{(1)}(x) + 1) + [\partial^2_{\beta} \ln y^{(1)}(x)]\} \).

In order to obtain the Grüneisen parameter we have also to determine the \((\partial M/\partial T)_H\). Therefore we have firstly to calculate the magnetization \(M = -(\partial f/\partial H)_T\) from (7),

$$M = \frac{1}{\beta}(K \ast \partial_H \ln B \bar{B})(0),$$

(14)

which is written in terms of the auxiliary function \(\partial_H \ln B(x) = b(x)/(b(x) + 1)\{[\partial_{\beta} \ln b(x)]\} \) and likewise for the other auxiliary functions) that are now derivatives with respect to the magnetic field. These new auxiliary functions are solutions of the following system of linear integral equations:

$$
\begin{pmatrix}
\partial_H \ln y^{(1/2)}(x) \\
\vdots \\
\partial_H \ln y^{(s-1/2)}(x) \\
\partial_{\beta} \ln b(x) \\
\partial_{\beta} \ln \bar{b}(x)
\end{pmatrix}
= \mathcal{K} \ast 
\begin{pmatrix}
\partial_H \ln Y^{(1/2)}(x) \\
\vdots \\
\partial_H \ln Y^{(s-1/2)}(x) \\
\partial_H \ln B(x) \\
\partial_H \ln \bar{B}(x)
\end{pmatrix},
$$

(15)

The derivative of the magnetization with respect to temperature for constant magnetic field \((\partial M/\partial T)_H = -\beta^2(\partial M/\partial \beta)_H\) can be finally obtained from (14), with the result

$$\frac{\partial M}{\partial T} = (K \ast \partial_H \ln B \bar{B})(0) - \beta(K \ast \partial^2_{\beta H} \ln B \bar{B})(0),$$

(16)

where \( \partial^2_{\beta H} \ln B(x) = [b(x)/(b(x) + 1)]\{[\partial_{\beta} \ln b(x)]\} \) which should satisfy

$$
\begin{pmatrix}
\partial^2_{\beta H} \ln y^{(1/2)}(x) \\
\vdots \\
\partial^2_{\beta H} \ln y^{(s-1/2)}(x) \\
\partial^2_{\beta H} \ln b(x) \\
\partial^2_{\beta H} \ln \bar{b}(x)
\end{pmatrix}
= \mathcal{K} \ast 
\begin{pmatrix}
\partial^2_{\beta H} \ln Y^{(1/2)}(x) \\
\vdots \\
\partial^2_{\beta H} \ln Y^{(s-1/2)}(x) \\
\partial^2_{\beta H} \ln B(x) \\
\partial^2_{\beta H} \ln \bar{B}(x)
\end{pmatrix},
$$

(17)

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3. The Grüneisen parameter and entropy

In this section we will present the results for the Grüneisen parameter, which is closely related to the magnetocaloric effect. We will also show the results for the entropy and the isentropes in the \((H,T)\) plane.

First we show in figure 1 the Grüneisen parameter \(\Gamma_H\) as a function of magnetic field for some spin values \(s = 1/2, 1, 3/2, 2\) and \(5/2\). Note that the result for the case \(s = 1/2\) was calculated in [10]. For the temperature \(T = 0.05\), we can see that the transition to saturation at \(H_c^{(s)} = 2/(s + 1/2)\) is signalled by sign changes of the Grüneisen parameter from negative to positive values toward the higher field values. For higher temperatures, like \(T = 0.5\), we note that these sign changes move away from the zero-temperature saturation field, which separates the antiferromagnetic and ferromagnetic phases. Finally, if we go further to higher temperatures, e.g. \(T = 5\), one can see that all the characteristic behaviour has disappeared, which implies that the thermal fluctuations are already strong enough to drive the system to excited states where no quantum phase transition effects can be seen. The maxima and minima in figure 1 scale with \(s\) in approximately the same way as the zeros. Moreover, there is a small structure at low magnetic fields and low temperatures (figure 1(a)) which is due to the singular nature of the point \((H = 0)\) of the isotropic integrable spin chains [10] and also due to the additional terms in the Hamiltonian (5) for \(s > 1\).

We show in figure 2 the entropy and the isentropes for the spin-\(s\) chain in the \((H,T)\) plane for \(s = 1, 3/2, 2\) and \(5/2\). The quantum phase transitions are indicated by the isentropes which are tilted towards the quantum critical point [9] showing minima near to \(H_c^{(s)}\) or equivalently the entropy peaks at the critical point. This accumulation of entropy near to the critical point indicates that the system is maximally undecided as regards which ground state to choose [9]. Moreover the Grüneisen parameter, which is proportional to the slope of the isentropes \((\partial T/\partial H)\), has a different sign on each side of the quantum critical point, as we have shown on figure 1. Besides, the isentropes are very steep near to the critical point, indicating the existence of a large magnetocaloric effect.

It is worth noting that besides the usual bilinear exchange interaction that appears in the standard spin-\(s\) Heisenberg chain, the integrable spin-\(s\) Hamiltonian (5) also has biquadratic and higher order spin exchange interactions. These additional terms produce different scalings of the maxima, minima and zeros as compared with [7]. Furthermore the spin-\(s\) Heisenberg chain and the integrable spin-\(s\) Hamiltonian have different classical limits [18].

4. Conclusion

In this paper we have studied the magnetocaloric effect for the integrable spin-\(s\) Hamiltonian, which includes higher order exchange interactions. We have calculated the Grüneisen parameter in the thermodynamic limit as a function of the magnetic field and temperature. We have also obtained the entropy and isentropes in the \((H,T)\) plane.

The quantum critical points \(H_c^{(s)}\) have been identified through the minima of the isentropes and the sign changes of the Grüneisen parameter as a function of the magnetic field. Our results are in agreement with the previous results for the \(s = 1/2\) case [10].

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Figure 1. The Grüneisen parameter $\Gamma_H$ for different values of the spin for (a) $T = 0.05$, (b) $T = 0.5$ and (c) $T = 5$.

Although the existence of the biquadratic and/or higher order exchange interaction has been investigated in recent times, it was generally assumed that these interactions are small for real systems [19]. This view was supported by many experimental results until the first experiment on the 1D spin-1 vanadium oxide [20] LiVGe$_2$O$_6$, which was 

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Figure 2. Entropy \(S(H,T)\) for \(s = 1, 3/2, 2\) and \(5/2\). The isentropes are for \(S = 0.1, 0.2, \ldots, 1.6\).

quantitatively explained using the spin-1 bilinear–biquadratic chain [20]. Later on, the biquadratic exchange term was considered as an effective mechanism for the description of many different compounds [21].

In addition to that, the \(SU(3) (SU(4))\) integrable Hamiltonian, which has biquadratic (and bicubic) exchange interactions, has been successfully used to describe thermal and magnetic properties of real compounds [22], e.g \(\text{Ni(C}_2\text{H}_8\text{N}_2)\text{Ni(CN)}_4\).

In view of that, we hope that our exact results will be useful for understanding future experimental results for quasi-one-dimensional systems. Alternatively, our results could be used as benchmarks for numerical methods used in the study of non-integrable high spin chains in direct applications. We also believe that our results could be further extended to the case of the alternating spin-(\(S_1, S_2\)) chain [23].

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