Thermodynamics of the $S = 1$ spin ladder as a composite $S = 2$ chain model

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A special class of $S = 1$ spin ladder hamiltonians, with second-neighbor exchange interactions and with anisotropies in the z-direction, can be mapped onto one-dimensional composite $S = 2$ (tetrahedral $S = 1$) models. We calculate the high temperature expansion of the Helmholtz free energy for the latter class of models, and show that their magnetization behaves closely to that of standard XXZ models with a suitable effective spin $S_{\text{eff}}$, such that $S_{\text{eff}}(1 + S_{\text{eff}}) = \langle \vec{S}_i^2 \rangle$, where $\vec{S}_i$ refers to the components of spin in the composite model.

It is also shown that the specific heat per site of the composite model, on the other hand, can be very different from that of the effective spin model, depending on the parameters of the hamiltonian.

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Many materials have been described by low-dimensional spin models such as XXZ, ladder, tetrahedral, dimmer chain, and mixed spin models. Different predictions are obtained from one-dimensional and quasi-one-dimensional models that can be verified experimentally; e.g., the $S = 1/2$ antiferromagnetic Heisenberg chain is a gapless model, whereas the even-legged antiferromagnetic Heisenberg ladder model has a gap in its energy spectrum. Attention has also been drawn to composite spin models; for instance, the $T = 0$ phase diagram for the

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This composite spin model is equivalent to the tetrahedral $S = 1/2$ model – applied to the study of the properties of the tellurate materials $Cu_2Te_2O_5Cl_5$ and $Cu_2Te_2O_5Br_5$. On the basis of experimental results it was argued that these materials could be appropriately described by the noninteracting tetrahedral $S = 1/2$ model. In Ref. we obtained the high temperature expansion of the Helmholtz free energy of the tetrahedral $S = 1/2$ model up to order $\beta^5$.

A common feature shared by all composite spin models is that the modulus of the spin at each site of the chain is not constant; instead, one has a random distribution throughout the chain. The presence of spin $S = 0$ in a given site of the chain can be interpreted as nonmagnetic impurity at that site.

By the appropriate design of molecules, it is possible to obtain a variety of spin systems. One example is the organic compound BIP-TENO, found to be a $S = 1$ spin ladder. At $T = 0$ this compound exhibits a plateau-like anomaly at 1/4 of the saturation magnetization, which has attracted much attention due to its full quantum nature. In Ref. a quasi one-dimensional spin model with second- and third-neighbor antiferromagnetic exchange interactions suitably explains the mechanism of the 1/4 magnetization plateau of this material; it does not include any anisotropy in the $z$-direction, though. Numerical analysis has been applied to study its phase diagram at $T = 0$; even in the absence of third-neighbor interactions the magnetization plateau is shown to be present.

In Ref. we presented a method to calculate the coefficients of the cummulant expansion of the Helmholtz free energy, in the thermodynamic limit, of any chain model whose hamiltonian satisfy periodic boundary conditions, possess invariance under spatial discrete translations and include interactions between nearest neighbors.

By a suitable choice of constants in the hamiltonian of Ref., the $S = 1$ ladder with second-neighbor interactions ($S = 1$ tetrahedral model, cf. model $B$ in Ref.); at each site, spin- 1/2 degrees of freedom are replaced by those of a fundamental spin- 1) can be mapped onto a family of one-dimensional composite $S = 2$ chain models. In the present work, we increase the parameter space of the model in Ref. by introducing anisotropies in the $z$-direction, calculate the high-temperature expansion of its Helmholtz free energy and compare its thermodynamics, in the
same regime of temperature, to the standard (irreducible representation) spin-$S$ XXZ model. The high-temperature expansion (or \(\beta\)-expansion, where \(\beta = 1/kT\), \(k\) is the Boltzmann constant and \(T\) is the absolute temperature) of the Helmholtz free energy for the composite \(S = 2\) XXZ model is obtained by applying the method presented in Ref. [10]. From the analytical results we may obtain the thermodynamic functions of the model at high temperatures; in particular, the magnetization \(M\) as a function of the external magnetic field \(h\) and the specific heat per site \(C_L\) as a function of \(\beta\).

The Hamiltonian of the quasi-one-dimensional spin model is

\[
H_{Q-1D} = \sum_{i=1}^{N} \left[ J_0 [(\sigma_i, \tau_i) \Delta_0 + \frac{1}{2} (\Delta_0 - 1) ((\sigma_i^z)^2 \otimes 1_\tau + 1_\sigma \otimes (\tau_i^z)^2)] + J [(\sigma_i, \sigma_{i+1}) \Delta \otimes 1_\tau + (\sigma_i, \tau_{i+1}) \Delta + (\tau_i, \sigma_{i+1}) \Delta + 1_\sigma \otimes (\tau_i, \tau_{i+1}) \Delta] - h (\sigma_i^z \otimes 1_\tau + 1_\sigma \otimes \tau_i^z) \right],
\]

and it is subject to periodic boundary conditions. We use the same notation as in Ref. [6]: \((A_l, B_k)_{\Delta} \equiv A_l^x \otimes B_k^x + A_l^y \otimes B_k^y + \Delta A_l^z \otimes B_k^z\), with \(A_l \equiv (A_l^x, A_l^y, A_l^z)\) and \(B_k \equiv (B_k^x, B_k^y, B_k^z)\), introducing the anisotropy in the \(z\)-direction. For \(\Delta_0 = 1\) and \(\Delta = 1\), \((1)\) equals to the sum of Hamiltonians \((2)\) and \((3)\) of reference [8] for the \(S = 1\) ladder with second-neighbor exchanges \((J_3 = 0)\), for the special case \(J_1 = J_2\). The distinct \(S = 1\) variables \(\sigma_i\) and \(\tau_i\) are related to the \(\rho\)- and \(r\)-lines of the dumb-bell, respectively (cf. Fig.1 of Ref. [6]).

We define the composite spin operators \(\vec{S}_i\) at the \(i\)-th site as \(\vec{S}_i = \vec{\sigma}_i \otimes 1_\tau + 1_\sigma \otimes \vec{\tau}_i\). Here, \(1_\sigma\) and \(1_\tau\) are the identity operators in \(\sigma\)- and \(\tau\)-space, respectively. Using the composite spin \(\vec{S}_i\), the tetrahedral \(S = 1\) Hamiltonian \((1)\) is rewritten as a composite \(S = 2\) chain Hamiltonian

\[
H_{Q-1D} = \sum_{i=1}^{N} \left[ -2J_0 1 + g(S_i, S_i) + J (S_i^+ S_{i+1}^- + S_i^- S_{i+1}^+ + \Delta S_i^z S_{i+1}^z) - h S_i^z + d(S_i^z)^2 \right],
\]

where \(g \equiv \frac{d_0}{2}, d \equiv \frac{d_0}{2} (\Delta_0 - 1), S_i^\pm \equiv \frac{1}{\sqrt{2}} (S_i^x \pm i S_i^y),\) and \(1\) is the identity operator, represented by a \(9 \times 9\) identity matrix. The block matrix representations of the composite spin operators in \((2)\), in the basis of eigenstates of \(S_i^z\) and \(\vec{S}_i^2\), are
\[
S_i^z = \begin{bmatrix}
\Sigma_{(2)}^z & 0 & 0 \\
0 & \Sigma_{(1)}^z & 0 \\
0 & 0 & \Sigma_{(0)}^z
\end{bmatrix}
\text{ and } S_i^+ = \begin{bmatrix}
\Sigma_{(2)}^+ & 0 & 0 \\
0 & \Sigma_{(1)}^+ & 0 \\
0 & 0 & \Sigma_{(0)}^+
\end{bmatrix},
\]

where the \( \Sigma \) square matrices refer to the different spin sectors.

\[
\Sigma_{(2)}^z = \begin{bmatrix}
-2 & 0 & 0 & 0 & 0 \\
0 & -1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 \\
0 & 0 & 0 & 0 & 2
\end{bmatrix}, \quad \Sigma_{(2)}^+ = \begin{bmatrix}
0 & 0 & 0 & 0 & 0 \\
\sqrt{2} & 0 & 0 & 0 & 0 \\
0 & \sqrt{3} & 0 & 0 & 0 \\
0 & 0 & \sqrt{3} & 0 & 0 \\
0 & 0 & 0 & \sqrt{2} & 0
\end{bmatrix},
\]

\[
\Sigma_{(1)}^z = \begin{bmatrix}
-1 & 0 & 0 \\
0 & 0 & 0 \\
0 & 0 & 1
\end{bmatrix}, \quad \Sigma_{(1)}^+ = \begin{bmatrix}
0 & 0 & 0 \\
1 & 0 & 0 \\
0 & 1 & 0
\end{bmatrix},
\]

\[
\Sigma_{(0)}^z = \begin{bmatrix}
0
\end{bmatrix}, \quad \Sigma_{(0)}^+ = \begin{bmatrix}
0
\end{bmatrix}.
\]

We point out that the operator \( \vec{S}_i^2 \) is a constant of the motion, although the hamiltonian (2) can be interpreted as a mixture of 3 kinds of spin \((S = 0, 1 \text{ and } 2)\), randomly distributed along the chain, with its probability depending on the constants of the hamiltonian and on the temperature.

An interesting limit of the hamiltonian (2) is \( g = J_0/2 \to 0 \), for finite values of \( d \equiv J_0 \Delta \). In this limit it acquires a single-ion anisotropy term.

As in Ref.[6], the presence of a spin \( S = 0 \) in a site of the chain can be interpreted as a nonmagnetic impurity at that site. The model thus encompasses the presence of randomly distributed impurities along the chain, without hindering the application of the method of Ref.[10], since the hamiltonian (2) has only nearest-neighbor interactions and is invariant under spatial translations.

Appendix A presents the \( \beta \)-expansion of the Helmholtz free energy \( W_{Q-ID} \) of the composite \( S = 2 \) XXZ model, up to order \( \beta^6 \). Although this expansion has a large number of terms, it is
easily differentiated by any symbolic computer language, yielding the thermodynamic functions of the tetrahedral $S=1$ model.

For finite temperatures the results are insensitive to the sign of $J$. If we redefine the parameters of the Hamiltonian (2) in units of $J$, the expression \( W_{Q-1D} \) becomes an expansion in \( \beta J \). For the sake of simplicity, we choose $J=1$ in what follows.

As we are discussing the case of the quasi one-dimensional model (the tetrahedral $S=1$ model) onto a chain model, it is interesting to compare the high-temperature thermodynamic properties of the latter, to those of the standard spin-$S$ XXZ model, for distinct values of $S$.

The free energy $W_{Q-1D}$ and the mean value of the squared norm of spin $\langle \vec{S}_i^2 \rangle$, for the $S=1$ ladder model with second-neighbor exchange interactions, are related by $\langle \vec{S}_i^2 \rangle = \frac{\partial W_{Q-1D}}{\partial g}$, for $g \equiv \frac{J_0}{2}$ and $d \equiv \frac{d_0}{2}(\Delta_0 - 1)$. $\langle \vec{S}_i^2 \rangle$ is a function of temperature and of the parameters of the Hamiltonian (2). At $\beta = 0$, the universal value $\langle \vec{S}_i^2 \rangle = 4$ is obtained, since in this limit of temperature we have $N$ independent spins with equal probability to be at $S=0, 1$ or 2.

Fig.1 shows $\langle \vec{S}_i^2 \rangle$ as a function of $\beta$ for two sets of values for the parameters of the composite model. $\langle \vec{S}_i^2 \rangle$ is not very sensitive to the value of $h$, within the range of $h$ where its $\beta$-expansion is a good approximation. We let $h=0$ in Fig.1a, in Fig.1b we have $\Delta = -0.3, g = 0.5$ and $d = -0.35$; and in Fig.1c $\Delta = 1, g = -0.5$ and $d = 0$. For the sake of comparison, Fig.1 also shows straight horizontal lines that correspond to the squared norms of spin per site for the standard XXZ model with $S=3/2$ and 2.

Fig.2 shows the entropy $S$ as a function of $\beta$, in units of Boltzmann’s constant ($S = \beta^2 \frac{\partial W}{\partial \beta}$), for the same set of parameter values as in Fig.1. In both cases the entropy of the tetrahedral $S=1$ model is higher than the entropy of the composite $S=2$ XXZ model. This result agrees with the fact that the number of degrees of freedom of the composite $S=2$ model is higher than that of the standard (irreducible) $S=2$ XXZ model.

In reference [12] Rojas et al. derived the high temperature expansion of the Helmholtz free energy $W_S$ of the standard spin-$S$ XXZ model, for arbitrary value of $S$ ($S$ being semi-integer or integer), up to order $\beta^6$. From their result, we obtain the expansion of the magnetization ($M$) of this family of models ($M = -\frac{\partial W}{\partial h}$). Appendix B shows this expansion up to order $\beta^6$. Postulating the validity of expansion (B1) for real positive values of $S$, we define an effective spin
FIG. 1: Expectation values of the squared norm of spin $\langle \vec{S}_i^2 \rangle$ as a function of $\beta = 1/kT$ for the composite $S = 2$ model (solid lines) and the standard spin-$S$ model, with $S = 3/2$ (dashed lines) and $S = 2$ (dot-dashed lines), for a vanishing magnetic field $h$. The values of parameters of the Hamiltonian (2) have been chosen as (a) $\Delta = -0.3$, $g = 0.5$ and $d = -0.35$ and (b) $\Delta = 1$, $g = -0.5$ and $d = 0$ (no anisotropy in the $z$-direction).

value $S_{\text{eff}}$ such that $S_{\text{eff}}(S_{\text{eff}} + 1) = \langle \vec{S}_i^2 \rangle$ where $\langle \vec{S}_i^2 \rangle$ relates to the composite $S = 2$ model.

Obviously, the effective spin depends on the values of the parameters of the theory (see Fig.1) and, in general, it is neither integer nor semi-integer. Fig.3a compares the magnetization of the tetrahedral $S = 1$ model and that of the effective XXZ model at $\beta = 0.2$, for $\Delta = 1, g = -0.5$ and $d = 0$. Fig.3b shows the percent error of the two curves in Fig.3a. Such error is less than 1.3% for $h \in [0, 1.4]$.

This similarity of behavior is not shared, in general, by the specific heat per site $C_L$ ($C_L = -\beta^2 \frac{\partial^2 \langle \mathcal{H} \rangle}{\partial \beta^2}$), as shown in Fig.4.
Fukushima et al. \cite{13} calculated the $\beta$-expansion of the specific heat per site of the spin-$S$ XXZ model, for arbitrary (semi-integer or integer) values of $S$, up to order $\beta^{11}$. Proceeding similarly as done for the magnetization, we postulate the validity of their expansion of the specific heat per site to any real positive value of $S$. Fig 4a shows the specific heat per site $C_L$ as a function of $\beta$ for the tetrahedral $S = 1$, the standard $S = 3/2$ and the effective $S_{eff}$ XXZ models; parameter values $h = 0$, $\Delta = -0.3$, $g = 0.5$ and $d = -0.35$ are the same as in Fig 1a. At high temperatures the curves are close: for $\beta \in [0.13, 0.27]$ the percent error is smaller than 5%, but for $\beta \sim 0$ it goes up to 27%.

Fig 4b was obtained for the same values of parameters used in Fig 1b, that is, $h = 0$, $\Delta = 1$, $g = -0.5$ and $d = 0$. The $C_L$ curves for the effective and the composite $S = 2$ models are...
\[ \beta = 0.2, \Delta = 1, g = -0.5 \text{ and } d = 0 \]

FIG. 3: The solid line in Fig 3a shows the magnetization \( M \) as a function of the external magnetic field \( h \) at \( \beta = 0.2 \) and for the following values of parameters of the composite \( S = 2 \) XXZ model\( ^2 \): \( \Delta = 1, \)

\( g = -0.5 \) and \( d = 0 \). The dashed line is the magnetization curve for the effective \( S_{\text{eff}} \) XXZ model. Fig 3b shows the percent error of the two curves in Fig 3a as a function of \( h \).

very different: the percent error for \( \beta \in [0, 0.2] \) varies from 20\% at \( \beta = 0 \), to 41.8\% at \( \beta = 0.2 \). Although there are \( S = 0 \) and \( S = 1 \) sites in a composite \( S = 2 \) XXZ chain, its specific heat is larger than that of a standard \( S = 2 \) chain, for \( \beta > 0.15 \).

In summary, we applied the method of Ref.\[10\] to calculate the high temperature expansion (\( \beta \)-expansion), up to order \( \beta^6 \), of the Helmholtz free energy of a special class of quasi one-dimensional models, the \( S = 1 \) ladders with second neighbor exchange interactions (the tetrahedral \( S = 1 \) models\[11\]). We have increased the parameter space of this class of hamiltonians by introducing anisotropies along the \( z \)-direction. This class of quasi one-dimensional
models can be mapped onto one-dimensional composite $S = 2$ XXZ models, with spins $S = 0, 1$ and 2 randomly distributed along the chain. At high temperatures, the thermodynamic properties of the composite $S = 2$ XXZ model and the standard spin-$S$ XXZ model are expected to differ, in principle; this is the case of the specific heat. However, a somewhat surprising result is that the magnetization of the tetrahedral $S = 1$ model follows that of an effective irreducible spin $S_{\text{eff}}$ model very closely (up to a percent error smaller than 2%). The effective spin is such that $S_{\text{eff}}(S_{\text{eff}} + 1) = \langle \vec{S}_i^2 \rangle$, and $\langle \vec{S}_i^2 \rangle$ is the expectation value of the squared norm of spin per site of the composite $S = 2$ XXZ model. The function $\langle \vec{S}_i^2 \rangle$ is a real-valued continuous function;
$S_{eff}$ may not be either integer or semi-integer.

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APPENDIX A: THE HELMHOLTZ FREE ENERGY OF THE TETRAHEDRAL $S = 1$ MODEL

The following expression for the high-temperature expansion up to order $\beta^6$ of the Helmholtz free energy refers to the composite $S = 2$ model (that is, the tetrahedral $S = 1$ model), whose dynamics is driven by the Hamiltonian (2). It is valid for any real values of $J_0, g, J, \Delta, d$ and $h$. (Observe that these values may be positive, null or negative). When $g = \frac{J_0}{2}$ and $d = \frac{J_0}{2} (\Delta_0 - 1)$, it yields the free energy of the Hamiltonian (1), for the $S = 1$ ladder model with second-neighbor interactions.

$$W_{Q-1D} = -\frac{\ln(9)}{\beta} + W_0 + W_1 \beta + W_2 \beta^2 + W_3 \beta^3 + W_4 \beta^4 + W_5 \beta^5 + W_6 \beta^6 + O(\beta^7), \quad (A1)$$

where

$$W_0 = -2 J_0 + \frac{4d}{3} + 4g \quad (A2)$$

$$W_1 = \frac{16 d g}{9} - \frac{8 g^2}{3} - \frac{8 J^2 \Delta^2}{9} - \frac{2 h^2}{3} - \frac{10 d^2}{9} - \frac{16 J^2}{9} \quad (A3)$$

$$W_2 = \frac{32 d^2 g}{27} - \frac{8 d g^2}{9} + \frac{64 J^2 \Delta^2 g}{27} - \frac{8 g^3}{9} + \frac{8 h^2 g}{9} + \frac{10 d h^2}{9} + \frac{46 d^3}{81}$$

$$- \frac{4 J^3 \Delta}{9} + \frac{16 J \Delta h^2}{9} + \frac{128 g J^2}{27} + \frac{80 d J^2 \Delta^2}{27} - \frac{16 d J^2}{27} \quad (A4)$$

$$W_3 = \frac{-146 J^4}{81} + \frac{512 d g J^2}{81} + \frac{32 J^3 \Delta d}{81} - \frac{32 J^2 \Delta^2 g^2}{81} - \frac{116 J^4 \Delta^2}{81}$$

$$- \frac{128 h^2 J \Delta g}{27} + \frac{104 J^2 \Delta^2 h^2}{27} + \frac{32 g J^3 \Delta}{27} - \frac{32 h^2 d^2}{27} - \frac{23 h^2 d^2}{27} + \frac{64 d g^3}{27} - \frac{64 J^2 \Delta^2 d g}{27} + \frac{4 h^2 g^2}{9} + \frac{20 h^2 J^2}{27} - \frac{34 J^4 \Delta^4}{27} - \frac{128 J^2 \Delta^2 d^2}{27}$$

$$- \frac{64 g^2 J^2}{81} + \frac{140 d^2 J^2}{81} + \frac{140 g^2 d^2}{81} + \frac{16 g^4}{9} + \frac{32 g d^4}{81} + \frac{h^4}{18} - \frac{160 h^2 J \Delta d}{27} + \frac{17 d^4}{162} \quad (A5)$$
\[ W_4 = \frac{664 J^3 \Delta^3 h^2}{27} + \frac{448 J^2 \Delta^2 d^2 h^2}{27} + \frac{256 J \Delta h^2 d^2}{27} - \frac{17 d^3 h^2}{81} \]
\[ \frac{-178 d J^4}{243} - \frac{58 J^2 \Delta}{243} - \frac{19 h^4 d}{243} + \frac{29 J^2 \Delta}{243} - \frac{44 J^2 d^3}{243} - \frac{100 d^2 J^3 \Delta}{243} \]
\[ -\frac{1538 d J^4}{243} - \frac{16 J^2 \Delta}{243} - \frac{172 d J^2 h^2}{243} + \frac{784 J^2 \Delta^2 d^2}{243} + \frac{428 J^2 \Delta^4 d^4}{243} \]
\[ -\frac{280 J^4 \Delta h^2}{81} - \frac{191 d^6}{243} - \frac{32 g d J^3 \Delta}{81} - \frac{64 g J^2 \Delta^2 d^2}{27} + \frac{352 J^2 \Delta^2 h^2 g}{81} \]
\[ + \frac{544 g J^2 \Delta^2 d^2}{81} + \frac{64 J \Delta h^2 g^2}{81} + \frac{320 J^4 \Delta^4 g}{27} - \frac{16 J^3 \Delta g^2}{81} - \frac{140 d h^2 g^2}{81} \]
\[ -\frac{928 J^3 \Delta^2 g}{81} - \frac{128 J^2 \Delta^2 g^3}{81} + \frac{200 g d}{27} + \frac{352 g d^4}{243} - \frac{8 h^4 g}{27} + \frac{428 g^2 d^3}{243} \]
\[ -\frac{16 d^2 g^3}{27} - \frac{32 h^2 g^3}{27} + \frac{176 g J^4}{27} - \frac{256 J^2 g^3}{27} + \frac{40 g^5}{27} + \frac{16 g d^2 h^2}{27} - \frac{320 d J^2 g^2}{27} \]
\[ -\frac{1568 d^2 J^2 g}{243} - \frac{352 g J^2 h^2 d g}{81} + \frac{128 J \Delta h^2 d g}{9} \]  
(A6)

\[ W_5 = \frac{298 J^2 d^2 h^2}{243} + \frac{2728 J^3 \Delta^2 d^2 h^2}{243} + \frac{3656 d J^3 \Delta^3 h^2}{243} - \frac{10256 d J^3 \Delta^3 h^2}{243} - \frac{1568 J \Delta h^2 d^3}{243} \]
\[ + \frac{128 J \Delta h^4}{27} + \frac{955 d^2 h^2}{972} + \frac{91 d^2 h^4}{108} - \frac{14827 J^6 \Delta^6}{1215} + \frac{3763 J^6 \Delta^4}{3645} - \frac{5959 J^2 d^4}{3645} \]
\[ + \frac{19 J^2 h^4}{81} + \frac{4601 J^2 d^4}{3645} + \frac{4861 J^6 \Delta^2}{81} - \frac{49 h^2 J^4}{243} - \frac{1220 d^2 g^4}{27} - \frac{100 g^4 h^2}{81} \]
\[ + \frac{2440 J^4 \Delta^2 h^2}{243} + \frac{376 d J^5 \Delta^3}{1215} + \frac{11216 J^4 \Delta^2 d^2}{1215} + \frac{92 J^2 \Delta^2 h^4}{27} + \frac{1532 J^2 \Delta^2 d^4}{729} \]
\[ - \frac{4088 d J^5 \Delta}{3645} + \frac{1397 d^6}{8748} + \frac{13 h^6}{1620} + \frac{4213 J^6}{10935} + \frac{808 J^3 \Delta d^3}{3645} - \frac{1828 J^4 \Delta^4 d^2}{243} \]
\[ + \frac{3650 J^4 \Delta^2 h^2}{243} - \frac{3776 J^2 \Delta^2 g^2 h^2}{27} + \frac{5152 g J^2 \Delta^2 d^3}{1215} + \frac{544 J^2 \Delta^2 g^2 h^2}{729} \]
\[ + \frac{11008 J^2 \Delta^2 d^2 g^3}{729} + \frac{2500 J^2 \Delta^4 g d}{243} + \frac{1600 J^2 g d^2 h}{243} + \frac{26144 d g J^3 \Delta^2}{729} \]
\[ + \frac{176 J^3 \Delta^2 g}{729} + \frac{5068 J \Delta h^2 g}{729} + \frac{64 J^3 \Delta d g^3}{27} + \frac{256 J \Delta h^2 g^3}{729} \]
\[ + \frac{7936 J^3 \Delta^3 g^2}{729} + \frac{320 J \Delta h^4 g}{27} - \frac{256 g^6}{729} + \frac{3664 J^2 d^2 g^2}{135} + \frac{18640 J^4 \Delta^2 g^2}{729} \]
\[ + \frac{704 h^2 g^3 d^3}{27} + \frac{16 h^2 d^2 h^2}{27} + \frac{128 J^2 \Delta^2 g^3}{729} + \frac{1184 g J^5 \Delta}{729} + \frac{592 J^5 \Delta^3 g}{729} \]
\[ + \frac{512 g J^3 \Delta}{729} + \frac{496 J^2 \Delta^2 h^2}{243} - \frac{64 J^3 \Delta g^3}{729} + \frac{9472 J^2 d^4 g^3}{27} + \frac{56 g^6 J^3 \Delta^4}{243} \]
\[ + \frac{448 J^2 d^2 g^3}{81} + \frac{104 g d h^4}{81} + \frac{214 d^2 h^2 g^2}{135} + \frac{512 g^5 d}{243} + \frac{256 J^2 g^4}{729} + \frac{9656 g^2 J^4}{729} \]
\[ + \frac{17 J^2 g^4}{81} + \frac{7696 g^4 d^3}{243} + \frac{101 h^2 d^4 g^3}{3645} + \frac{2296 g^6 d^2}{27} - \frac{1376 J^2 \Delta^2 g d h^2}{27} \]
\[ + \frac{128 J^2 \Delta h^2 J^2 \varepsilon J^2 g}{27} - \frac{1088 h^2 d^2 J \Delta g}{81} \]  
(A7)
\[ W_6 = \frac{20581 J^2 a^5}{10935} - \frac{1397 h^2 d^5}{2916} + \frac{371 J^5 \Delta^5}{7290} + \frac{1871 J^6 d}{1215} - \frac{3064 J \Delta h^2 d^4}{729} + \frac{63404 J^4 \Delta^4 h^2 d}{729} + 2492 J^2 \Delta^4 h^2 d^4 - 1900 J^3 \Delta h^2 d^2 \\
+ \frac{25384 J^2 \Delta^2 h^2 d^3}{729} + \frac{72121 J^3 \Delta^3 h^2 d^2}{729} - \frac{2492 J^2 \Delta^4 h^2 d^4}{81} - \frac{19426 J^2 \Delta^2 d^2}{81} + \frac{121261 J^6 \Delta^4 d^4}{729} + \frac{2222 J^2 h^2 d^3}{10935} + \frac{841 h^4 d^3}{972} + \frac{10935}{10935} \\
+ \frac{11 h^6 d}{108} + \frac{8341 J^7 \Delta}{10935} + \frac{14456 J^7 \Delta^3}{10935} - \frac{5689 J^4 d^3}{10935} - \frac{84224 J^2 g^5}{3645} + \frac{32989 d^5 g^2}{10935} + \frac{11588 d^4 g^3}{2187} - \frac{9424 d^2 g^5}{3645} + \frac{256 h^2 g^2}{135} + \frac{2212 d^2 g^3}{729} + \frac{11176 d^6 g}{10935} \\
+ \frac{15058 J^6 g}{10935} - \frac{37408 J^4 g^3}{2187} + \frac{20 h^4 g^3}{27} + \frac{4 h^6 g}{45} + \frac{2576 d^6 g}{405} - \frac{33004 J^6 \Delta^2 d}{10935} + \frac{4928 J^4 \Delta^2 d^3}{2187} + \frac{3416 J^4 \Delta^4 d^4}{2187} - \frac{1208 J^3 \Delta^3 h^2 d^2}{81} - \frac{1252 J^5 \Delta^5 d^2}{3645} \\
+ \frac{96854 J^5 \Delta^5 h^2}{3645} - \frac{266 J^5 \Delta h^2}{243} - \frac{230 J^5 \Delta^4 h^4}{81} - \frac{4636 J^2 \Delta^2 d^5}{729} + \frac{8126 J^6 \Delta^6 d}{2187} + \frac{8201 d^7}{18560} - \frac{17192 J^2 \Delta^5 d^2 g}{729} - \frac{128 J^2 \Delta^2 d^4}{243} - \frac{6656 J^2 \Delta^2 d^2 g^2}{243} + \frac{48640 J^4 \Delta^4 h^2 g}{729} \\
+ \frac{19840 J^2 \Delta^2 h^2 d^3}{729} + \frac{5920 J^3 \Delta^3 h^2 d^2}{243} + \frac{352 J^4 \Delta^4 d^2 g}{729} + \frac{16208 J^4 \Delta^4 d^2 g}{729} + \frac{6136 J^2 \Delta^2 h^4 g}{243} + \frac{11080 J^5 \Delta d g}{2187} - \frac{37376 J^3 \Delta h^2 d^2 g}{729} + \frac{8432 J^3 \Delta d^3 g}{10935} \\
+ \frac{4048 J^3 \Delta d^2 d^2 g}{2187} + \frac{256 J^3 \Delta \Delta^2 h^2 d g}{2187} + \frac{6224 J^5 \Delta^2 d^2 g}{729} + \frac{5392 J^2 h^2 d^2 g}{729} + \frac{52576 J^3 \Delta^2 h^2 g}{729} - \frac{56002 J^6 \Delta^2 d^2 g}{729} - \frac{68088 J^3 \Delta^2 d^2 g}{243} - \frac{1472 J^4 \Delta^4 h^2 g}{243} + \frac{494 J^2 \Delta^2 d g}{243} + \frac{63280 J^2 d^2 g^2}{243} + \frac{200 J^2 h^4 d^2 g}{3645} + \frac{48968 J^2 d^4 g}{2187} + \frac{19576 J^3 \Delta^2 d^2 g}{2187} \\
+ \frac{31744 J^2 d^4 g^4}{729} + \frac{1220 h^2 d^3 g^4}{243} + \frac{1396 J^6 \Delta^2 d^2 g}{405} + \frac{23872 J^4 \Delta^4 d^3 g}{2187} + \frac{8384 J^2 d^2 g^3}{243} + \frac{6464 J^2 \Delta^2 h^2 g^3}{729} + \frac{30176 J^4 \Delta^2 d g}{729} + \frac{928 J^4 \Delta d^2 g}{729} + \frac{448 h^4 d^2 g}{1148 h^2 d^4 g} + \frac{9788 J^5 \Delta^3 d^2 g}{243} \\
+ \frac{11 h^4 d^2 g^2}{243} - \frac{22712 J^6 \Delta^4 d^4}{243} + \frac{26912 J^6 \Delta^6 d^4}{243} + \frac{64 J^3 \Delta^4 d^4}{2187} + \frac{42112 J^2 \Delta^2 d^4 g}{3645} + \frac{78424 J^2 d^4 g^3}{2187} + \frac{3848 h^2 d^3 g^2}{729} + \frac{202 h^2 d^3 g}{243} - \frac{8224 J^4 \Delta^4 d^3 g^3}{729} + \frac{368 g^7}{135} + \frac{108544 J^3 \Delta^1 h^2 d^2 g}{729} + \frac{10040 J^1 \Delta h^2 d^2 g}{729} + \frac{7552 J^3 \Delta h^2 d^2 g^2}{243} + \frac{22016 J^6 \Delta^2 h^2 d^2 g}{729} + \frac{1216 J^2 \Delta^2 h^2 d^2 g^2}{243} + \frac{18416 J^2 \Delta^2 h^2 d^2 g^2}{243} + \frac{6080 J^3 \Delta h^2 d^4 g}{243} + \frac{57488 J^3 \Delta h^2 d^2 g}{729} (A8)
APPENDIX B: HIGH TEMPERATURE EXPANSION OF THE MAGNETIZATION OF THE SPIN-S XXZ MODEL

From the high temperature expansion of the Helmholtz free energy $W_S$ of the irreducible spin-S XXZ model in Ref. [12], we obtain the magnetization $M$ as function of the squared norm of the spin $s(s+1)$, up to order $\beta^6$:

$$M = -\frac{\partial W_S}{\partial h} = M_1 \beta + M_2 \beta^2 + M_3 \beta^3 + M_4 \beta^4 + M_5 \beta^5 + M_6 \beta^6 + O(\beta^7)$$ (B1)

where the coefficients $M_j$ are polynomials in $s(s+1)$,

$$M_1 = \frac{h s(s+1)}{3}$$ (B2)

$$M_2 = -\left(\frac{4}{45} h d + \frac{2}{9} \Delta h\right) s^2 (s+1)^2 + \frac{h d s(s+1)}{15}$$ (B3)

$$M_3 = -\left(\frac{4}{135} h - \frac{8}{945} h d^2 - \frac{14}{135} \Delta h - \frac{16}{135} \Delta h d\right) s^3 (s+1)^3$$
$$-\left(\frac{1}{30} h + \frac{4}{105} h d^2 + \frac{1}{45} h^3 + \frac{1}{15} \Delta h + \frac{4}{45} \Delta h d\right) s^2 (s+1)^2$$
$$-\left(-\frac{1}{42} h d^2 + \frac{1}{90} h^3\right) s (s+1)$$ (B4)

$$M_4 = -\left(-\frac{8}{4725} h d + \frac{128}{4725} \Delta h d^2 - \frac{344}{4725} \Delta^2 h d + \frac{92}{2025} \Delta h - \frac{16}{225} \Delta h d - \frac{16}{14175} h d^3\right) s^4 (s+1)^4$$
$$-\left(-\frac{8}{135} \Delta h^3 - \frac{352}{4725} \Delta h d^2 - \frac{16}{2025} h^3 d - \frac{32}{225} h^2 d^3 - \frac{16}{675} \Delta^3 h\right) s^3 (s+1)^3$$
$$-\left(-\frac{386}{4725} \Delta^2 h d - \frac{16}{1575} h d - \frac{19}{675} h h\right) s^2 (s+1)^2$$
$$+\frac{2}{945} h^3 d + \frac{1}{75} \Delta h - \frac{4}{135} \Delta h^3 + \frac{32}{1575} \Delta^2 h d + \frac{64}{1575} \Delta h d^2\right) s (s+1)$$ (B5)
\[
M_s = -\left( \frac{32}{2835} \Delta h d - \frac{64}{1701} \Delta^3 h d - \frac{718}{42525} \Delta^4 h \\
- \frac{4}{2835} h - \frac{64}{42525} \Delta h d^3 - \frac{64}{2835} \Delta^2 h d^2 + \frac{848}{42525} \Delta^2 h + \frac{32}{93555} h d^4 - \frac{32}{14175} h d^2 \right) \\
+ \frac{128}{14175} \Delta h d + \frac{176}{2835} \Delta^3 h d + \frac{352}{14175} \Delta h d^3 + \frac{64}{945} \Delta^2 h d^2 + \frac{32}{525} \Delta h^3 d \\
+ \frac{383}{42525} \Delta^2 h + \frac{229}{14175} \Delta^4 h + \frac{358}{4725} \Delta^2 h^3 \right) s^3 (s+1)^3 - \left( \frac{8}{14175} h d^2 - \frac{16}{31185} h d^4 + \frac{16}{567} h - \frac{4}{525} h^3 \right) \\
- \frac{128}{14175} h^3 d^2 - \frac{1}{210} h - \frac{158}{14175} h^3 - \frac{2}{945} h^5 - \frac{38}{1575} \Delta h d - \frac{16}{567} \Delta^3 h d \\
- \frac{652}{14175} \Delta h d^3 - \frac{8}{135} \Delta^2 h d^2 - \frac{136}{14175} \Delta h^3 d - \frac{271}{14175} \Delta^2 h - \frac{64}{14175} \Delta^4 h \\
+ \frac{424}{14175} \Delta^2 h^3 \right) s^3 (s+1)^3 - \left( \frac{41}{6300} h d^2 + \frac{1}{17} h d^4 - \frac{11}{3150} h^3 d^2 + \frac{1}{840} h - \frac{37}{6300} h^3 \right) \\
- \frac{1}{630} h^5 + \frac{13}{1575} \Delta h d + \frac{2}{945} \Delta^3 h d + \frac{4}{189} \Delta h d^3 + \frac{1}{63} \Delta^2 h d^2 - \frac{128}{4725} \Delta h^3 d \\
+ \frac{1}{315} \Delta^2 h + \frac{1}{3780} \Delta^4 h - \frac{23}{4725} \Delta^2 h^3 \right) s^2 (s+1)^2 \\
- \left( \frac{5}{792} h d^4 - \frac{1}{2520} h^5 + \frac{1}{180} h^3 d^2 \right) s (s+1) \\
\text{(B6)}
\]
\[ M_0 = -\left( -\frac{1592}{1488375} \right) h d \]
\[ + \frac{16064}{49116375} h d^3 + \frac{1472}{638512875} h d^5 - \frac{8336}{893025} \Delta^2 h d + \frac{12032}{893025} \Delta^3 h d^2 \]
\[ - \frac{35072}{49116375} h d^4 + \frac{70424}{4465125} \Delta^4 h d + \frac{2528}{893025} \Delta h^- \Delta^2 h + \frac{8}{178605} \Delta^3 h + \frac{5132}{893025} \Delta^5 h \]
\[ + \frac{5792}{1964655} \Delta^2 h d^3 + \frac{1856}{1488375} \Delta h d^2 \]
\[ s^6 (s + 1)^6 - \left( -\frac{8}{1488375} \right) h d - \frac{304}{606375} \Delta h d^3 \]
\[ + \frac{16}{4725} h^3 d + \frac{24512}{70945875} h d^6 - \frac{32}{66825} h^3 d^3 - \frac{16}{893025} \Delta^2 h d - \frac{1696}{33075} \Delta^3 h d^2 \]
\[ - \frac{44416}{16377125} h d^4 - \frac{5942}{165375} \Delta^4 h d + \frac{7628}{893025} \Delta h + \frac{2}{6615} \Delta^3 h + \frac{64}{2835} \Delta h^3 \]
\[ - \frac{2656}{297675} \Delta^5 h - \frac{992}{14175} \Delta^3 h^3 - \frac{128}{4725} \Delta h d^2 - \frac{1328}{14175} \Delta^3 h d^3 - \frac{17152}{654885} \Delta^2 h d^3 \]
\[ + \frac{496}{165375} \Delta h d^2 \]
\[ s^6 (s + 1)^5 - \left( \frac{1259}{992250} h d + \frac{1168}{606375} h d^3 + \frac{4}{675} h^3 d \right) \]
\[ + \frac{1}{4725} h^3 d - \frac{2096}{70945875} h d^5 - \frac{4}{1575} h^3 d^3 + \frac{1607}{59355} \Delta^2 h d + \frac{2048}{33075} \Delta^3 h d^2 \]
\[ + \frac{12864}{1128645} \Delta h d + \frac{13882}{496125} \Delta^4 h d + \frac{1543}{1190700} \Delta h + \frac{17137}{1190700} \Delta^3 h + \frac{139}{4725} \Delta h^3 \]
\[ + \frac{1}{4725} \Delta^5 h = \frac{656}{422525} \Delta^3 h^3 + \frac{2}{175} \Delta h^5 + \frac{64}{1575} \Delta h d^2 + \frac{16}{525} \Delta^2 h d^3 \]
\[ + \frac{96}{13475} \Delta^2 h d^3 + \frac{2158}{165375} \Delta h d^2 \]
\[ s^6 (s + 1)^4 - \left( \frac{253}{220500} h d - \frac{12071}{1819125} h d^3 \right) \]
\[ + \frac{1}{4725} h^3 d - \frac{42166}{7882875} h d^5 - \frac{194}{51975} h^3 d^3 + \frac{2}{4725} h^5 d - \frac{683}{33075} \Delta^2 h d \]
\[ - \frac{2606}{992250} \Delta^3 h d^2 - \frac{165736}{5457375} \Delta h d + \frac{8111}{992250} \Delta^4 h d + \frac{193}{133075} \Delta h - \frac{481}{66150} \Delta^3 h \]
\[ + \frac{142}{14175} \Delta^5 h + \frac{1}{1323} \Delta^5 h + \frac{152}{14175} \Delta^3 h^3 + \frac{44}{4725} \Delta h^5 + \frac{184}{14175} \Delta h d^2 \]
\[ + \frac{563}{14175} \Delta^2 h d^3 - \frac{48809}{1091475} \Delta^2 h d^3 - \frac{2423}{110250} \Delta h d^2 \]
\[ s^6 (s + 1)^3 - \left( \frac{43}{88200} h d \right) \]
\[ + \frac{647}{1611700} h d^3 - \frac{31}{6300} h^3 d + \frac{177571}{18918900} h d^5 - \frac{32}{6237} h^3 d^3 - \frac{19}{18900} h^5 d \]
\[ + \frac{4}{1225} \Delta^2 h d + \frac{74}{33075} \Delta^3 h d^2 + \frac{4553}{636825} \Delta h d^4 + \frac{37}{66150} \Delta^4 h d^2 + \frac{13}{14700} \Delta h \]
\[ + \frac{17}{22050} \Delta^3 h = \frac{11}{3150} \Delta h^3 + \frac{1}{26460} \Delta^5 h - \frac{2}{2835} \Delta^3 h^3 + \frac{11}{4725} \Delta h^5 + \frac{4}{189} \Delta h^3 d^2 \]
\[ - \frac{1}{135} \Delta^2 h d^3 + \frac{4553}{363825} \Delta^2 h^3 d^3 + \frac{11}{1440} \Delta h d^2 \]
\[ s^2 (s + 1)^2 \]
\[ - \left( \frac{5}{1188} h^3 d^3 - \frac{1}{1800} h^5 d - \frac{691}{163800} h d^3 \right) s (s + 1) \]

(B7)

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