We present a numerical study of thermodynamical properties of dimerized frustrated Heisenberg chains down to extremely low temperatures with applications to CuGeO$_3$. A variant of the finite temperature density matrix renormalization group (DMRG) allows the study of the dimerized phase previously unacessible to ab initio calculations. We investigate static dimerized systems as well as the instability of the quantum chain towards lattice dimerization. The crossover from a quadratic response in the free energy to the distortion field at finite temperature to nonanalytic behavior at zero temperature is studied quantitatively. Various physical quantities are derived and compared with experimental data for CuGeO$_3$ such as magnetic dimerization, critical temperature, susceptibility and entropy.

I. INTRODUCTION

The investigation of low dimensional quantum spin systems has attracted widespread and general interest. Active research is performed on a large class of magnetic materials, experimentally as well as theoretically. Up to date, an enormous understanding of the low-energy physics of quasi-one dimensional systems such as spin-Peierls, Haldane and ladder systems has been reached. Still it is a challenging task to investigate especially the low temperature regime of these systems, because for $T$ close to zero thermal fluctuations are strongly reduced and quantum fluctuations become dominant.

The recently developed transfer-matrix DMRG, which combines White’s DMRG idea with the transfer-matrix approach is particularly suited for this task because the thermodynamic limit in quantum space can be performed exactly. Most other numerical techniques such as the “traditional” Hamiltonian DMRG or exact diagonalization are restricted to either zero temperature or to rather large temperatures. Quantum Monte Carlo algorithms also can only be applied to systems finite in both quantum and Trotter direction. Furthermore, the sign problem for frustrated systems is a rather sophisticated point associated with the latter approach.

In this paper we investigate the thermodynamics of dimerized frustrated Heisenberg chains, which are believed to model appropriately the spin degrees of freedom of, for instance, the inorganic spin-Peierls compound CuGeO$_3$. The purpose of this paper is twofold. First, we want to show that a density matrix renormalization group treatment of a “lattice path integral formulation” for general spin chains with dimerization and frustration is possible. Within this approach we will understand qualitatively and quantitatively the instability of one-dimensional frustrated antiferromagnetic Heisenberg systems towards dimerization at finite temperature. Second, we want to show that many of the thermodynamic properties of CuGeO$_3$ can be understood within the one-dimensional adiabatic approach. At least with respect to the location of $T_{sp}$, the entropy and the susceptibility down to temperatures of 5K the role of higher dimensional magnetic couplings is less relevant.

The paper is organized as follows. Computational aspects and the model Hamiltonian are given in section II. In section III we analyze the dependence of the free energy on the dimerization and the crossover from analytical to non-analytical behavior in the limit of vanishing temperature. We compare our numerical findings to theoretical results based on scaling arguments. In addition we present the temperature dependence of the order parameter within the adiabatic approach. In section IV we show results for the magnetic susceptibility as well as the entropy which compare excellently with the experimental data for CuGeO$_3$. Summary and conclusion are given in section V.

II. MODEL AND METHOD

The dominant magnetic interactions in CuGeO$_3$ are due to Heisenberg spin exchange between $Cu^{2+}$ ions along the $c$-axis of the crystal with strong nearest ($J$) and next-nearest neighbor ($\alpha J$) interactions. As usual, we assume a linear dependence of the nearest neighbor exchange integral on the local structural deformation. The commonly used Hamiltonian in adiabatic approximation reads

$$\hat{H} = \sum_i \left\{ J((1+\delta_i)S_i S_{i+1} + \alpha S_i S_{i+2}) + \frac{K}{2} \mathbf{s}_i^2 - h \mathbf{s}_i \right\},$$

(1)

where $\mathbf{S}_i$ are spin 1/2 operators, $\delta_i = (-1)^i \delta$ denotes the modulation of the exchange coupling in the dimerized phase ($\delta > 0$ is assumed) and $h = g \mu_B H_{ex}$ represents the effective external magnetic field. The last two terms
in $[\delta]$ are the elastic energy associated with the lattice distortion and the Zeeman energy.

In order to have a translationally invariant description we combine each two spin 1/2 to an effective four state object resulting in a model with only nearest neighbor interaction. A similar strategy has been adopted in Ref. [8] to cast a system with next-nearest neighbor interaction in a form suitable for applications of the transfer matrix DMRG algorithm. Firstly, the elastic part of the Hamiltonian is neglected pending further notice, i.e. $K = 0$, since it only enters as a trivial constant in all energies and can be added finally.

After chequerboard decomposition $[\delta]$ of the effective four state problem the partition function is calculated by means of the quantum transfer matrix $T_M$. In the thermodynamic limit all physical quantities are determined by the largest eigenvalue $\Lambda$ of $T_M$ and the corresponding left and right eigenstate. More precisely, the free energy per site of the spin-1/2 chain reads

$$f = -\frac{1}{T} \ln \Lambda.$$  

Expectation values of local operators like the internal energy $u$, magnetization $m$ or nearest neighbor correlation $\langle S_i S_{i+1} \rangle$ etc. can be expressed in terms of the eigenstates (see $[\delta]$ and for a general reference to transfer matrix formalisms e.g. $[4]$). The quantum transfer matrix $T_M$, $\Lambda$ and the eigenvectors are calculated by iterative augmentation in Trotter direction within an application of the DMRG concept as in $[\delta],[\delta]$. For all calculations we kept 24 states in the renormalization step and chose $(TM)^{-1} = 0.05$.

III. GENERAL RESULTS

First we calculate the free energy $f(T, \delta)$ for the system $[\delta]$ for a series of fixed distortions $\delta_i = (-1)^i \delta$. From general principles we expect analytic behavior for any finite temperature, i.e.

$$f(T, \delta) = f(T, 0) + \frac{1}{2!} a(T) \delta^2 + \frac{1}{4!} b(T) \delta^4 + O(\delta^6),$$  

where the odd powers in $\delta$ disappear due to the obvious symmetry $\delta \to -\delta$. The coefficient $a(T)$ of $\delta^2$ is the reciprocal of the static “dimerization susceptibility”. Hence, a zero in this coefficient signals a structural transition.

Numerically we determine the coefficient by analyzing

$$A(T, \delta) = \frac{1}{J} \left[ -\frac{1}{\delta} \frac{\partial f(T, \delta)}{\partial \delta} + K \right] = \frac{\langle S_i S_{i+2} \rangle - \langle S_i S_{i+3} \rangle}{2 \delta}$$  

which in the limit $\delta \to 0$ is simply denoted by $A(T)$. Note that $A$ is independent of $K$. In Fig.1 we show DMRG results for the temperature dependence of $A(T, \delta)$ for various $\delta$ in the case $\alpha = 0$.

The relation $a(T) = K - JA(T)$ holds exactly, but we are restricted to finite $\delta$ in our numerics since the error in $A(T, \delta)$ scales with $1/\delta^2$. (Determining $A(T)$ directly from $f(T, \delta) - f(T, 0)$ would even involve an error of order $1/\delta^2$.) In the sense of a multi-point formula we can assume an expansion like $[\delta]$ up to order $\delta^{2n}$ to hold exactly, and calculate the corresponding $n$ coefficients by considering the function $A(T, \delta)$ for $n$ different values of $\delta$. In this way we obtain reliable approximations for the functions $a(T), b(T), \ldots$. In the present work we employed a $n = 3$ point formula and used the three smallest dimerizations accessible.

[FIG. 1. $A(T, \delta)$ as defined in the text versus temperature for $\alpha = 0$ and $\delta = 0.15, 0.1, 0.05, 0.04, 0.03, 0.01$ (from bottom to top) and the extrapolated $A(T)$ (dashed line). The inset shows a log-log plot of $(A(T) + c)$ with $c = -1.14$ (dashed line) together with a line with slope -1 (thin solid line).]

Here we are particularly interested in $A(T)$ at low temperature showing a divergence at $T = 0$. This singularity is caused by the failure of $[\delta]$ at zero temperature. From $[\delta],[\delta]$ and also from scaling relations of the quantum critical Heisenberg chain $[\delta]$ we know for $\alpha < \alpha_c$ ($\alpha_c \approx 0.2412$ $[\delta],[\delta]$) that $f(0, \delta) - f(0, 0) \approx \delta^{4/3}$. For $\alpha > \alpha_c$ the quantum chain shows spontaneous magnetic dimerization as well as an excitation gap which leads to $f(0, \delta) - f(0, 0) \approx \delta$.

More quantitatively, we first define a temperature variable $t = f(T, 0) - f(0, 0)$. The singular part of the free energy in dependence of $t$ and $\delta$ is denoted by $f(t, \delta) = f(T, \delta) - f(0, 0)$. Then, we expect the following scaling relation

$$\tilde{f}(t, \delta) = \frac{1}{t^{\xi}} \hat{f}(tl^x, \delta l^y).$$  

(See e.g. $[\delta]$ as a general reference.) The exponents $x$ and $y$ are to be determined. From $[\delta]$ we derive in the usual manner $\hat{f}(t, \delta) = t^{1/\xi} \hat{f}(1, \delta/t^{\nu/\xi})$. Fixing $\delta = 0$
directly implies $x = 1$ due to the definition of $t$. Next we use the fact that $\tilde{f}(0, \delta) \approx \delta^0$ which implies $f(1, z) \approx z^n$ for large $z$ and furthermore $y = 1/\eta$. Lastly we note

$$A(T) = \frac{\partial^2}{\partial \delta^2} \tilde{f}(t, 0) = t \frac{1}{12/n} \frac{\partial^2}{\partial \delta^2} \tilde{f}(1, 0) \approx t^{1-\frac{2}{n}}. \quad (5)$$

Fig. 1 displays $A(T, \delta)$ for $\alpha = 0$ and various $\delta$ and $A(T)$ (dashed line) derived from the curves with the lowest dimerization. As expected the low-temperature behavior of the free energy for vanishing dimerization is found to be $t = T^2$ with an extrapolated groundstate energy $f_0 = -0.443$. Here we have $\eta = 4/3$, thus we should observe $A(T) \approx 1/T$ at sufficiently low $T$. This is excellently confirmed by our numerics (see inset of Fig. 1). As the scaling relations only apply to the divergent terms we are allowed to subtract regular terms. For instance an additive constant for $A(T)$ does not change the scaling, but enlarges the temperature range where this sets in.

For overcritical frustration $\alpha > \alpha_c$ a similar scaling analysis can be performed. The main difference is the absence of quantum criticality due to the gap $\Delta$ of the elementary excitations.

\begin{equation}
A(T, \delta(T)) = \frac{K}{T}, \quad (6)
\end{equation}

i.e. the intersection of $A(T, \delta)$ for fixed $\delta$ with the constant $K/J$. The transition temperature $T_{\text{sp}}$ is defined by $\delta(T_{\text{sp}}) = 0$. For higher (lower) temperatures the free energy is increased (lowered) for non-vanishing $\delta$ corresponding to the uniform (dimerized) phase. For determining the spontaneous dimerization we use (6) rather than the free energy intersection whose accuracy is expected to be a factor $1/\delta$ worse.

In Fig. 3 the temperature dependence of the spontaneous dimerization $\delta(T)$ is depicted exemplarily for $\alpha = 0, K = 1.6J$ and $\alpha = 0.35, K = 2.4J$. The exponents at the critical temperature $T_{\text{sp}}$ are close to $1/2$ which is expected due to the mean-field treatment of the elastic degrees of freedom. The numerical analysis has been performed for a discrete set of parameters $\delta$ with maximum value 0.15 which appears to be an upper bound for the actual $\delta(T = 0)$ of both examples. The value is in agreement with earlier self-consistent calculations by means of the DMRG for zero temperature [2].

Moreover, the critical temperature as a function of the elastic constant as well as a function of the dimerization $\delta(T = 0)$ can be deduced from $A(T, \delta)$. The transition temperature of CuGeO$_3$ will be discussed in the following section.
Due to fluctuations in the real system while our theoretical calculations indicate a sharp transition point. Using an elastic constant of $K = 11J$ the calculated critical temperature is equal to the experimentally determined value $T_{sp} = 14.4K$. Below $T_{sp}$ the susceptibility is systematically underestimated. With $K = 10.2J$, the DMRG results perfectly coincide with experiment (see Fig. 3), but the transition takes place at about 15.2K. Of course, this is a natural effect due to the meanfield approximation. A similar overestimation of $T_{sp}$ is observed by adjusting a square root behavior to the experimentally measured lattice dimerization [24].

In Fig. 3 the entropy $S(T, \delta(T))$ for $\alpha = 0.35$ is depicted. The consistency with the entropy bounds derived by an analysis of the specific heat was already mentioned in [23] for temperatures above 35K. The experimentally determined bounds are also respected for temperatures between $T_{sp}$ and 35K, below the critical temperature we observe deviations of about 5% with respect to the upper bound for $K = 11J$. Decreasing the elastic constant to $K = 10.2J$ with the consequences stated above the bounds are respected in the entire temperature range.

IV. APPLICATION TO CuGeO$_3$

Since the discovery of CuGeO$_3$ as the first inorganic spin-Peierls compound there have been numerous studies of appropriate sets of microscopic couplings [17,22,23]. Within the one dimensional adiabatic approach commonly used parameter are: $J \approx 160K$, $\alpha \approx 0.35$ and $\delta(T = 0) \approx 1.3\%$ [17,22,23]. These parameters were derived mainly by fitting the experimental susceptibility data in the uniform phase well above $T_{sp}$ and from the singlet-triplet gap (singlet-singlet gap [24]) at zero temperature. Note, that the entropy for these interaction parameters also satisfies bounds derived from the specific heat data [23].

Next we focus on a brief comparison to experimental data. Fig. 4 shows experimental and theoretical susceptibility data. The agreement for $\chi(T)$ with exact diagonalization ($L = 16$) of the non-dimerized frustrated Heisenberg chain (dashed line) and DMRG results using $K = 11J$ (circles), $K = 10.2J$ (crosses).

Now the low temperature regime is accessible for the first time by means of the transfer matrix DMRG. To derive the experimentally observed thermodynamics we have to set $K = 11J$ (10.2J) which implies a maximum dimerization of $\delta(T = 0) \approx 2.6\%$ (2.8%) and $\Delta_{ST} \approx 40K$ (42K). The larger dimerization compares well with recent results of Büchner et al. [26]. They conclude a minimum dimerization of 3% based on measurements of the pressure dependence of the exchange couplings together with the structural distortion. Interestingly, the larger saturation dimerization leads to a singlet-triplet gap close to the average gap $\Delta_{ST} \approx 44K$, which may be used within the one dimensional approach regarding the interchain interaction ($b$ direction) approximately [27].

Nevertheless, these elastic constants deviate from earlier $T = 0$ calculations, where $K = 18J$ ($\delta(T = 0) \approx 1.4\%$) is found to describe the zero temperature physics correctly [28]. In particular, the experimentally observed gap and the critical magnetic field at the D/I transition are reproduced for $K = 18J$. We have to use a smaller value for $K$ to obtain accordance with the experimental transition temperature. The apparent discrepancy of our finite $T$ calculations and the results in [28] may be ex-
plained by residual interchain interactions as discussed above.

\[ S_{\text{mag}} \text{[J/Kmole]} \]

FIG. 5. Entropy for CuGeO\textsubscript{3}. Comparison of experimentally determined bounds (solid lines) with DMRG results using \( K = 11J \) (circles) and \( K = 10.2J \) (crosses).

V. SUMMARY

By applying a quantum transfer matrix DMRG algorithm to the frustrated Heisenberg chain with fixed dimerization we calculated physical quantities down to temperatures of less than 0.05 in units of the coupling constant \( J \).

The results compare to analytical predictions based on scaling arguments with perfect agreement. In particular, we can clearly distinguish between the quantum critical case \((\alpha < \alpha_c)\) and overcritical frustration \((\alpha > \alpha_c)\) which are characterized by different divergence behavior of the \( \delta^2 \)–coefficient in the free energy. Furthermore, the instability towards dimerization can be understood within this numerical approach. It is the first calculation of the spin-Peierls temperature in the adiabatic model \([1]\) for realistic sets of parameters \( J, \alpha, K \) and the first quantitative investigation of the dimerized phase at finite temperatures.

Especially with respect to CuGeO\textsubscript{3}, taking the parameters \( J = 160K, \alpha = 0.35 \) established by high temperature studies and an elastic constant \( K = 11J \) \((10.2J)\), a critical temperature of \( T_{\text{SP}} \approx 14.4K \) \((15.2K)\) is found. Results from the latter parameter set are in perfect agreement with the experimental results, e.g. magnetic susceptibility (Fig. 3) and entropy (Fig. 5). The slight deviation in the value of \( T_{\text{SP}} \) can be probably traced back to the static treatment of the lattice dimerization which overestimates transition temperatures.

In general, our results extend the numerical analysis to much lower temperatures, including the dimerized phase.

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