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Surface effects in quantum spin chains

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Abstract
Chains of quantum spins with open ends and isotropic Heisenberg exchange are studied. By diagonalizing the Hamiltonian for chains of finite length N and obtaining all the energy eigenvalues, the magnetic susceptibility χ, the specific heat C_v, and the partition function Z can be calculated exactly for these chains. The high-temperature series expansions of these are then evaluated. For χ and C_v it is found that the terms in the series consist of three parts. One is the normal high-T series already known in great detail for the $N \to \infty$ ring (chain with periodic boundary conditions). The other two consist of a 'surface' term and a correction term of order $(1/T)^N$. The surface term is found as a series up to and including $(1/T)^8$ for spin $S = 1/2$ and 1. Simple Padé approximant formulae are given to extend the range of validity below $T = 1$.

1. Introduction and three atom chain

Quantum spin chains with isotropic Heisenberg exchange have been studied for many years. Most of this work deals with rings of atoms, i.e. chains with periodic boundary conditions. High-temperature series expansions were developed early on by Baker *et al* [1], and Domb and others [2, 3]. A summary of much of the early work can be found in Rushbridge *et al* [4]. For the spin $S = \frac{1}{2}$ chains the Bethe ansatz has enabled many properties to be calculated more directly from integral equations. In combination with analytic formulae from conformal field theory, valid at low T, extremely accurate and detailed numerical results are known [5, 6]. Using these the high-temperature series expansions have been calculated to very large numbers of terms (~50) in recent years [7, 8]. Of course, the Bethe ansatz is not directly applicable to chains with $S > \frac{1}{2}$, and direct calculation of the high-temperature series remains an important way to study these systems.

We shall refer to these results for closed chains with periodic boundary conditions in the limit that the number of atoms $N \to \infty$ as *bulk* results. In this paper chains with *open* ends are studied. These have not been studied in detail for spin-$\frac{1}{2}$ by Bethe ansatz methods, which in any case would not be relevant for $S > \frac{1}{2}$.

To illustrate the method first consider a chain of three spin-$\frac{1}{2}$ atoms with Hamiltonian

$$\mathcal{H} = J(\mathbf{s}_1 \cdot \mathbf{s}_2 + \mathbf{s}_2 \cdot \mathbf{s}_3). \quad (1)$$

Positive J indicates antiferromagnetic coupling and negative J ferromagnetic. The total z-component of spin, $S_T^z = s_1^z + s_2^z + s_3^z$, is a good quantum number.

The total number of states is $(2S + 1)^N$, in this case 8, with eigenvalues E_j and corresponding values of S_T^z denoted by m_j. These are shown in the table:

m_j	E_j
$\pm\frac{1}{2}$	$-1, 0, \frac{1}{2}$
$\pm\frac{3}{2}$	$\frac{1}{2}$

We define

$$Z_n = \sum_j (E_j)^n \mathrm{e}^{-\beta E_j},$$

where $\beta \equiv \frac{1}{T}$ and Boltzmann's constant k_B is taken as 1. The sums are over the eigenstates labelled by subscript j.

The quantities to be calculated as a function of temperature T are:

(1) The zero-field magnetic susceptibility:

$$\chi = \beta \frac{\sum_j m_j^2 \mathrm{e}^{-\beta E_j}}{Z_0}. \quad (2)$$

(2) The specific heat:

$$C_v = \beta^2 \frac{(Z_2 Z_0 - Z_1^2)}{Z_0^2}. \quad (3)$$

(3) The partition function:

$$Z \equiv Z_0. \quad (4)$$

For the susceptibility of the three spin-$\frac{1}{2}$ chain we obtain

$$\frac{\chi T}{N} = \frac{x^{-2} + 1 + 10x}{12(x^{-2} + 1 + 2x)}$$

where $x = \mathrm{e}^{-\beta/2}$. The high-temperature expansion of this is

$$\frac{\chi T}{N} = \frac{1}{4} - \frac{1}{12}\beta - \frac{1}{96}\beta^2 + \frac{1}{144}\beta^3 + \frac{7}{2304}\beta^4 - \frac{17}{46\,080}\beta^5 - \frac{617}{1105\,920}\beta^6 - \frac{253}{3870\,720}\beta^7 + \frac{4576}{61\,931\,520}\beta^8 + \frac{29549}{1114\,767\,360}\beta^9 + \cdots.$$

The power series in the ferromagnetic case with $J = -1$ is identical except that all odd powers of β have the sign of the coefficient reversed. The numerical results in this paper are presented for the antiferromagnetic case with $J = 1$ and figures are given both for this and for the ferromagnetic case with $J = -1$.

For the specific heat we have

$$C_v/N = \frac{(-x^{-2} + x)}{(x^{-2} + 1 + 2x)}$$

with high-temperature expansion

$= \frac{1}{8}\beta^2 + \frac{1}{16}\beta^3 - \frac{3}{128}\beta^4 - \frac{5}{192}\beta^5 - \frac{1}{768}\beta^6 + \frac{119}{20\,480}\beta^7 + \frac{2629}{1474\,560}\beta^8 - \frac{401}{516\,096}\beta^9 + \cdots$

and for the partition function

$$Z/N = 2(x^{-2} + 1 + 2x)/3$$

with high-temperature expansion

$= \frac{8}{3} + \frac{1}{2}\beta^2 + \frac{1}{12}\beta^3 + \frac{1}{32}\beta^4 + \frac{1}{192}\beta^5 + \frac{11}{11\,520}\beta^6 + \frac{1}{7680}\beta^7 + \frac{43}{2580\,480}\beta^8 + \frac{17}{9289\,728}\beta^9 + \cdots.$

In subsequent sections these results are extended to larger N and S.

2. Zero-field magnetic susceptibility

The Hamiltonian for general N is

$$\mathcal{H} = J \sum_{k=1}^{N-1} \mathbf{s}_k \cdot \mathbf{s}_{k+1}. \tag{5}$$

For values of $N > 3$ and/or for $S > 1/2$ the eigenvalues were obtained numerically, and the series calculated from these with the coefficients in the form of decimal numbers. Nevertheless, it is normally possible to identify the coefficients in rational form and this is necessary in order to obtain exact results for the general form of the coefficients. The rational numbers obtained when both N and β are large have very large numerators and denominators. They are believed to be correct for all values and agree with exact results where known. Also, the bulk results derived from them below are in agreement with known values [8]. Nevertheless, conversion of decimal numbers to rational numbers always admits the possibility of error.

Let $c_i(N)$ be the coefficient of β^i in the high-temperature series expansion of $\chi T/N$, where χ is the zero-field magnetic susceptibility for a chain of length N. We show in the table the $S = 1/2$ coefficients for $i \leqslant 5$ and $3 \leqslant N \leqslant 9$, although in fact they have been calculated for N up to 14 and for i up to 9. c_0 is not shown since it is always $1/4$.

N	c_1	c_2	c_3	c_4	c_5
3	$-\frac{1}{12}$	$-\frac{1}{96}$	$\frac{1}{144}$	$\frac{7}{2304}$	$-\frac{17}{46\,080}$
4	$-\frac{3}{32}$	$-\frac{1}{128}$	$\frac{1}{128}$	$\frac{1}{2304}$	$-\frac{101}{122\,880}$
5	$-\frac{1}{10}$	$-\frac{1}{160}$	$\frac{1}{120}$	$\frac{7}{384}$	$-\frac{1}{1200}$
6	$-\frac{5}{48}$	$-\frac{1}{192}$	$\frac{5}{576}$	$\frac{7}{2560}$	$-\frac{17}{18\,432}$
7	$-\frac{3}{28}$	$-\frac{1}{224}$	$\frac{1}{112}$	$\frac{13}{4608}$	$-\frac{53}{53\,760}$
8	$-\frac{7}{64}$	$-\frac{1}{256}$	$\frac{7}{768}$	$\frac{31}{10\,752}$	$-\frac{127}{122\,880}$
9	$-\frac{8}{72}$	$-\frac{1}{288}$	$\frac{1}{108}$	$\frac{3}{1024}$	$-\frac{37}{3840}$
N	$-\frac{(N-1)}{8N}$	$-\frac{1}{32N}$	$\frac{(N-1)}{96N}$	$\frac{(5N-4)}{1536N}$	$-\frac{(21N-41)}{15\,360N}$

The last line of the table gives the form for general N. For $i > 5$ the general form obtained is

$$c_6 = -\frac{(399N - 664)}{128 \times 5!N} \qquad c_7 = \frac{(320N - 1461)}{1024 \times 6!N}$$

$$c_8 = \frac{(11\,421N - 25\,778)}{1024 \times 8!N} \qquad c_9 = \frac{(74\,740N - 126\,454)}{4096 \times 9!N}.$$

Table 1. Table of coefficients in the high-T expansion of $\chi T/N$.

	$S=1/2$		$S=1$	
	χ_b	χ_s	χ_b	χ_s
c_0	$\frac{1}{2^2}$	0	$\frac{2}{3}$	0
c_1	$-\frac{1}{2^3}$	$\frac{1}{2^3}$	$-\frac{8}{3^2}$	$\frac{8}{3^2}$
$c_2*2!$	0	$-\frac{1}{2^4}$	$\frac{20}{3^3}$	$-\frac{52}{3^3}$
$c_3*3!$	$\frac{1}{2^4}$	$-\frac{1}{2^4}$	$\frac{32}{3^3}$	$\frac{16}{3^2}$
$c_4*4!$	$\frac{5}{2^6}$	$-\frac{1}{2^4}$	$-\frac{260}{3^4}$	$\frac{244}{3^4}$
$c_5*5!$	$-\frac{21}{2^7}$	$\frac{41}{2^7}$	$-\frac{4896}{3^5}$	$\frac{1616}{3^5}$
$c_6*6!$	$-\frac{399}{2^9}$	$\frac{83}{2^6}$	$\frac{11\,324}{3^5}$	$-\frac{3188}{3^4}$
$c_7*7!$	$\frac{320}{2^{10}}$	$-\frac{1461}{2^{10}}$	$\frac{67\,240}{3^4}$	$-\frac{237\,112}{3^5}$
$c_8*8!$	$\frac{11\,421}{2^{10}}$	$-\frac{12\,889}{2^9}$	$-\frac{600\,964}{3^6}$	$\frac{123\,356}{3^7}$
$c_9*9!$	$\frac{74\,740}{2^{12}}$	$-\frac{63\,227}{2^{11}}$	—	—

It is important to note, as can easily be checked, that the general form of $c_i(N)$ is valid only for $i \leqslant N$. This is also true for the values not shown.

It can now be seen that the general form of the coefficients consists of two parts, and we can write

$$c_i(N) = b_i + s_i/N$$

where b_i and s_i are constants independent of N. Since the series is for $\chi T/N$ the first term is a 'bulk' term giving a contribution to χ of order N, while the second term is a 'surface' or 'edge' term whose contribution to χ does not change with increasing N. Thus it can be concluded that the total susceptibility of a chain of length N consists of three parts:

$$\chi = N\chi_b + \chi_s + \chi_{corr}$$

where all three terms are functions of T: χ_b and χ_s are independent of N and χ_{corr} is a correction term of order $(\beta)^{N+1}$. The coefficients of the powers of β are given in table 1 for χ_b and χ_s.

The results are shown in figure 1 for the bulk susceptibility per spin and the surface susceptibility for both antiferromagnetic and ferromagnetic chains. These are calculated using the high-temperature expansions up to seventh, eighth and ninth powers of β and also simple 4/4 Padé approximants. The bulk results are of course the same as the exact results, known very accurately from the Bethe ansatz method, and these are also shown, taken from Eggert *et al* [5] and Klümper [6]. The power series are clearly well converged for $T > 1$ and the Padé approximant is accurate for $T \geqslant 0.6$.

The main feature of the result is that the surface susceptibility of the antiferromagnetic chain is the same sign as that of the bulk, whereas for the ferromagnetic chain the surface susceptibility is negative. These remarks apply to the temperature range where the series is clearly converged, i.e. not at low temperatures, although it seems quite probable that they would apply there also.

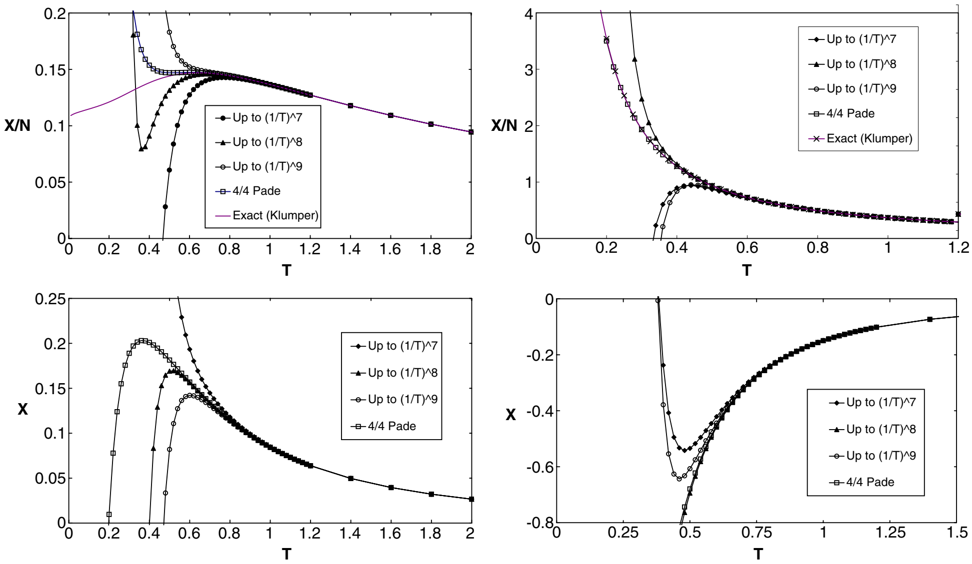

Figure 1. Bulk zero-field susceptibility per spin (top) and surface zero-field susceptibility (bottom) for open $S = 1/2$ chains. Antiferromagnetic (left) and ferromagnetic (right).

The surface susceptibility in the antiferromagnetic case rises more sharply than the bulk as $T \to 0$. Also the Padé approximant curve has a clear maximum, unlike the bulk case in which it diverges. There are not sufficient terms available to determine the low-temperature behaviour with any certainty but one might speculate that the Padé curves at this level of approximation which have a maximum may correspond to susceptibility which tends to 0 as $T \to 0$ while those which diverge may correspond to susceptibility which tends to a non-zero value. A plot of $\chi_s \times T$ for the antiferromagnet shows evidence of a peak at $T \approx 0.6$.

Spin-1 has also been investigated. Only chains up to $N = 9$ have been fully diagonalized. Nevertheless it is again possible to identify the first few terms in the series for both bulk and surface susceptibilities. These are also given in table 1. For the bulk susceptibility the 4/4 Padé approximants results are similar to the spin-$\frac{1}{2}$ case for both the antiferromagnetic and ferromagnetic chains, although with the curves shifted to higher temperatures. The same is true for the surface susceptibility in the ferromagnetic case, but for the antiferromagnet the Padé result diverges for $S = 1$, instead passing through a maximum as in the $S = \frac{1}{2}$ case. The results are shown in the appendix.

3. Specific heat

The specific heat is given by equation (3) and is calculated in essentially the same way as the susceptibility. The results for the $S = \frac{1}{2}$ and 1 antiferromagnetic chains are

$$C_v = NC_b + C_s + C_{corr}$$

where all three terms are functions of T: C_b and C_s are independent of N and C_{corr} is a correction term of order $(\beta)^{N+1}$. Each of C_b and C_s is obtained as a power series in β with coefficients given in table 2. For both $S = \frac{1}{2}$ and 1 the coefficients given are valid for all N except that c_8 and c_9 are valid only for $N \geqslant 4$. The resulting curves are shown in figure 2.

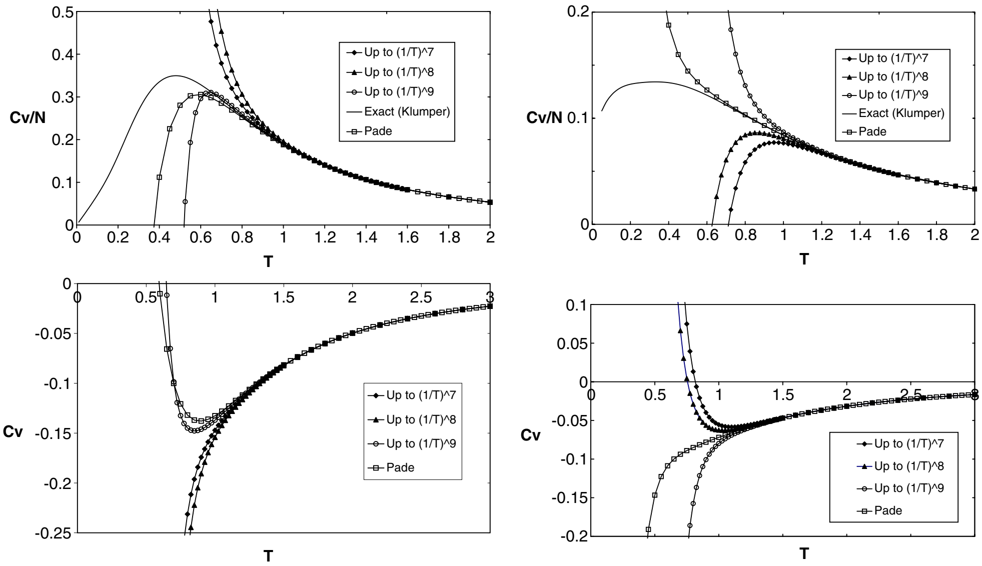

Figure 2. Bulk specific heat per spin (top) and surface specific heat (bottom) for open $S = 1/2$ chains. Antiferromagnetic (left) and ferromagnetic (right).

Table 2. Table of coefficients in the high-T expansion of C_v/N.

	$S = 1/2$		$S = 1$	
	C_b	C_s	C_b	C_s
c_0	0	0	0	0
c_1	0	0	0	0
c_2	$\frac{3}{2^4}$	$-\frac{3}{2^4}$	$\frac{4}{3}$	$-\frac{4}{3}$
c_3	$\frac{3}{2^5}$	$-\frac{3}{2^5}$	$\frac{2}{3}$	$-\frac{2}{3}$
$c_4 * 2!$	$-\frac{15}{2^7}$	$\frac{27}{2^7}$	$-\frac{40}{3^2}$	$\frac{56}{3^2}$
$c_5 * 3!$	$-\frac{45}{2^7}$	$\frac{75}{2^7}$	$-\frac{10}{3}$	$\frac{130}{3^3}$
$c_6 * 4!$	$\frac{63}{2^9}$	$-\frac{237}{2^9}$	$\frac{616}{3^3}$	$\frac{368}{3^2}$
$c_7 * 5!$	$\frac{2751}{2^{10}}$	$-\frac{6111}{2^{10}}$	$\frac{1603}{3^2}$	$-\frac{8729}{3^3}$
$c_8 * 6!$	$\frac{12\,753}{2^{12}}$	$-\frac{20\,853}{2^{12}}$	$-\frac{186\,392}{3^4}$	$\frac{134\,024}{3^3}$
$c_9 * 7!$	$-\frac{64\,545}{2^{11}}$	$\frac{178\,107}{2^{11}}$	$-\frac{312\,745}{3^3}$	$\frac{2007\,507}{3^4}$

Here the main feature is that the surface contribution to the specific heat is negative over the converged range for both the antiferromagnet and the ferromagnet. This can be understood in terms of the density of energy states for surface states being lower than for bulk states owing to the 'looser coupling' of the surface atoms which have only one neighbour.

Table 3. Table of partition function polynomials for $S = \frac{1}{2}$.

i	f_i
0	1
1	$-(N+1)$
2	N^2+5N-2
3	$-(N^3+12N^2+9N-14)$
4	$N^4+22N+75N^2-98N+40$
5	$-(N^5+35N^4+265N^3-35N^2-850N+1096)$
6	$N^6+51N^5+675N^4+1385N^3-6420N^2+5940N+1360$
7	—
8	—

The first few terms for the $S = 1$ series for the specific heat are also given in table 2. Again the main features are the same as for $S = \frac{1}{2}$. The results are shown in the appendix.

4. Partition function

The partition function equation (4) is again calculated in the same way. However, the results have a different form. Since Z is not a directly measurable (physical) quantity we might not expect the result to consist of a bulk, a surface and a correction term as for the susceptibility and the specific heat. The result is as follows. For a spin-$\frac{1}{2}$ antiferromagnetic chain of length N

$$Z = \sum_{i=0}^{\infty} c_i \beta^i \tag{6}$$

where

$$c_i = \frac{2^{N-2i}}{Ni!} f_i(N)$$

where $f_i(N)$ is a polynomial of degree i in N. The form of the f_i is given in table 3.

However, it is remarkable that these coefficients are valid for all $N \geqslant 3$, i.e. there is no correction of order β^i.

5. Conclusion

The main conclusion to be drawn is that there is clear evidence of well-defined surface effects in quantum spin chains with open ends. These become exact for infinite length chains but have corrections of order $\frac{1}{T}^k$ where $k \to \infty$ as the length $N \to \infty$. The relation between k and N depends on the spin length S and also on whether one considers the susceptibility or the specific heat. Because the terms in the high-temperature series expansion are calculated in this paper using a method which depends on full diagonalization of the Hamiltonian, only chains with $N \leqslant 14$ for $S = \frac{1}{2}$ and $N \leqslant 9$ for $S = 1$ were considered. The resulting series are somewhat limited and cannot be used for very low temperatures.

Nevertheless it is interesting to speculate whether the methods which have been used for the integrable $S = \frac{1}{2}$ chains with periodic boundary conditions might possibly be useful in determining these surface functions, at least for $S = \frac{1}{2}$.

Physically the most noticeable effects are the enhancement of the susceptibility of the antiferromagnetic chain and the decrease for the ferromagnetic chain. For the specific heat the surface term gives a decrease in both cases.

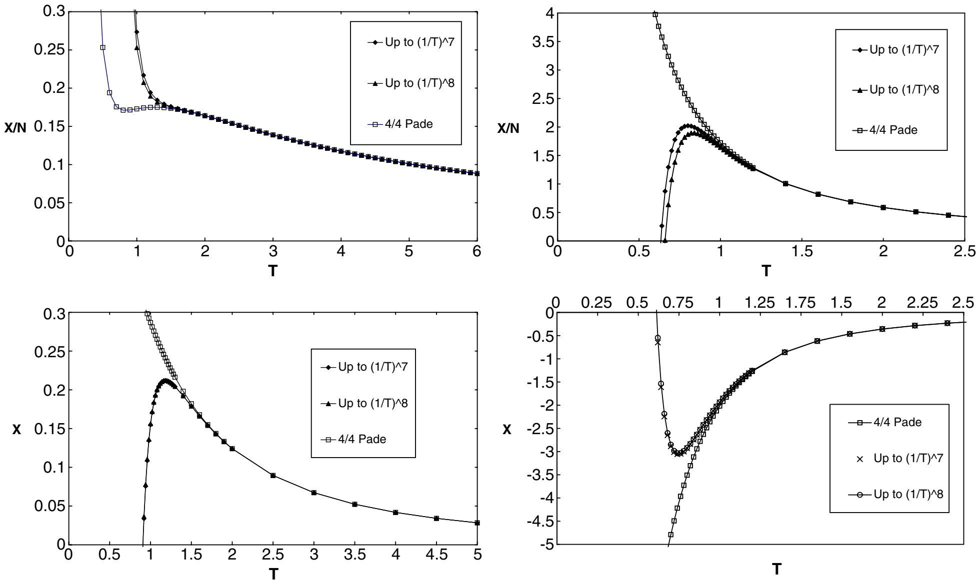

Figure A.1. Bulk zero-field susceptibility per spin (top) and surface zero-field susceptibility (bottom) for open $S = 1$ chains. Antiferromagnetic (left) and ferromagnetic (right).

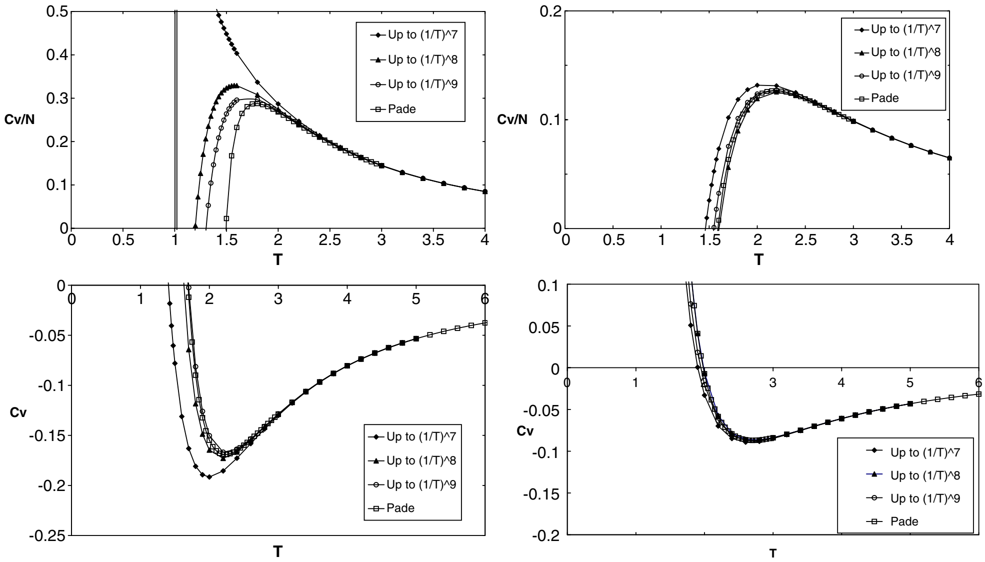

Figure A.2. Bulk specific heat per spin (top) and surface specific heat (bottom) for open $S = 1$ chains. Antiferromagnetic (left) and ferromagnetic (right).

The results for the partition function for $S = \frac{1}{2}$ do not have any direct consequence for physical measurements, but are perhaps interesting because of the way they give exact information about finite as well as infinite N.

Acknowledgments

I am very grateful to Andreas Klümper for supplying detailed exact bulk results for the susceptibility and the specific heat for both antiferromagnetic and ferromagnetic $S = 1/2$ chains. I am also grateful to N M Bogoliubov for useful background information.

Appendix

Figures A.1 and A.2 show the results for the susceptibility and the specific heat for $S = 1$.

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