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LETTER TO THE EDITOR

Magnetic specific heat of isotropic linear chains for $S \leqslant \frac{5}{2}$

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Abstract. Estimates are presented for the magnetic specific heat of an infinite chain of spins with isotropic nearest-neighbour exchange. The calculations are performed for $S = \frac{1}{2}, 1, \frac{3}{2}, 2$ and $\frac{5}{2}$. The results are presented graphically. A simple expression is used to represent the results for ferromagnetic as well as for antiferromagnetic interaction.

The one-dimensional arrangement of magnetically-coupled spins has received continuous theoretical attention during the last decades. (For a review see Lieb and Mattis (1966).) Recently interest has increased due to the success of experimentalists in growing crystals with nearly one-dimensional properties, for instance tetra methyl ammonium manganese chloride (TMMC) (Dietz *et al* 1971) and $CsMnCl_3 \cdot 2H_2O$ (CMC) (Smith and Freiberg 1968, Kobayashi *et al* 1973). The thermal behaviour of both salts was studied recently (Takeda 1974 and Kopinga *et al* 1975).

In general interpretation of specific heat data is obscured by a lack of information concerning the lattice contribution and by a lack of reliable estimates for the magnetic specific heat of the infinite lattice. Even in the case of one-dimensional arrangements the theoretical predictions for the specific heat and susceptibility of infinite-spin ensembles with $S > \frac{1}{2}$ are limited. In view of this and in order to interpret the recent experiments on CMC and TMMC we thought it worthwhile to start calculations on these arrangements.

We present here estimates for the specific heat of infinite chains for all spins up to $S = \frac{5}{2}$, obtained from cluster calculations. For experimental use we represent the results by an approximate formula that should be helpful in fitting procedures. The magnetic interaction will be isotropic and between nearest neighbours only, according to the Hamiltonian

$$\mathcal{H} = -2J \sum_{i=1}^{N-1} \boldsymbol{S}_i \cdot \boldsymbol{S}_{i+1}. \tag{1}$$

Eigenvalues of $\mathcal{H}$ are obtained by diagonalization of the corresponding matrix. To reduce the dimensions of the eigenvalue problems, basis functions were generated that are eigenfunctions of $T_z (= \Sigma S_{i_z})$ and that transform conforming to one of the irreducible representations of the symmetry group associated with $\mathcal{H}$. For a ring of N spins ($\mathcal{H}$ then contains the additional term $\boldsymbol{S}_1 \cdot \boldsymbol{S}_N$) this is the group D_N, while chains transform according to D_2. The maximum chain lengths used in the present calculations are $N = 11$, 7, 6, 5 and 4 for $S = \frac{1}{2}, 1, \frac{3}{2}, 2$ and $\frac{5}{2}$ respectively.

Once the eigenvalues are solved, the partition function can be calculated and consequently the specific heat per spin, C_N.

For rings and chains, C_N approaches the specific heat of an infinite chain (C_∞) in different ways. For rings there are no boundary effects but non-physical spin correlations

are allowed. Chains, on the other hand, suffer from boundary effects but are otherwise a fair representation of a one-dimensional system. To obtain a reliable estimate for C_∞ the information for different N should be extrapolated and we found chains more useful in this procedure than rings. The origin of a suitable extrapolation formula, as used in this work, stems from the theory of high-temperature series expansions (HTE) of C_N in powers of $\beta(=J/kT)$. The coefficient of the first term in this series (in β^2) is proportional to Tr ($\mathscr{H}^2$) and this in turn is proportional to the number of bonds in the finite chain. Thus, at high temperatures, C_N multiplied by $N/(N-1)$ will approximate the specific heat per spin in the limit $N \to \infty$ better than C_N itself.

With decreasing temperature, more terms in the series expansion become important and this simple extrapolation fails. However, it was proved (de Neef and de Jonge 1975) that the more general relation of the form

$$C_N = C_\infty(1-\alpha(T)/N) \tag{2}$$

holds for chains, as long as N is large enough to contain the largest graph that contributes appreciably to the HTE.

A convenient way of extrapolation is thus found in a plot of C_N against $1/N$. This technique works even for fairly low temperatures, since it turns out that chains that do not contain the largest graph deviate from the supposed linear relation (2) with alternating sign for N even and odd. Basically the method eliminates the boundary effects and is therefore not meaningful with ring calculations. All estimates of C_∞ presented here were therefore obtained from chains. The plots of C_N against $1/N$ were fitted to a straight line with a weighted least-squares criterion, and the squares sum was used as a measure for the uncertainty in the estimated limit. A demonstration of such a fit for $S = 1$ is shown in figure 1, for two temperatures. The full lines are best fits and the error bar corresponds to a 2σ interval (σ is the standard deviation).

Reliable results are obtained in this way for $S = \frac{1}{2}$ and $S = 1$ (de Neef and de Jonge 1974). For higher S the number of solvable chains decreases rapidly with increasing spin and application of the method to the case of $S = \frac{5}{2}$ alone, for instance, would not

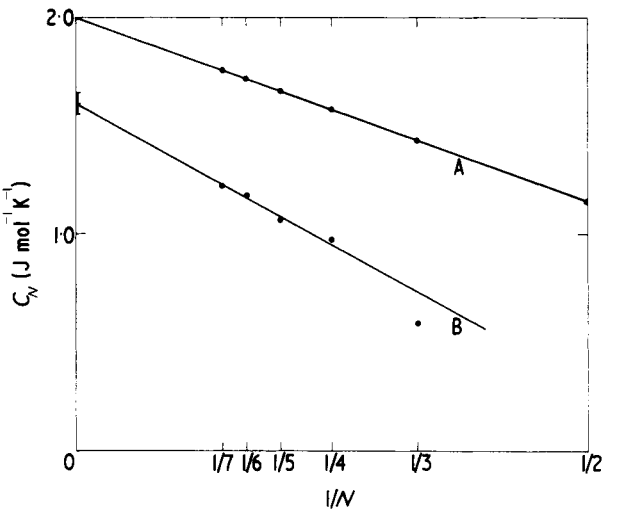

Figure 1. Plot of C_N against $1/N$ for chains with $S = 1$. The full circles represent the calculated specific heat. The full lines are best fits in the sense of least squares. A, $kT/J = 3$; B, $kT/J = 0{\cdot}5$.

be very trustworthy. However, comparison of the results with those obtained from the HTE makes us confident that the calculated error bounds are quite realistic, even for $S > 1$. Comparison with the results of Bonner and Fisher (1964) for $S = \frac{1}{2}$ and with those of Weng (1968) for $S = 1$ shows differences of the order of a few per cent near $T = T_m$ (the temperature for which C reaches a maximum). The results are displayed in figures 2 and 3 for ferromagnetic and antiferromagnetic interaction respectively, together with Fisher's (1964) result for the classical limit $S \to \infty$. The figures are conveniently scaled to a reduced temperature $\mathscr{T} = kT[JS(S+1)]^{-1}$. The curves are drawn in the temperature range where the estimated uncertainty is less than 4%. This error bound is found at the low-temperature side and the uncertainty is rapidly

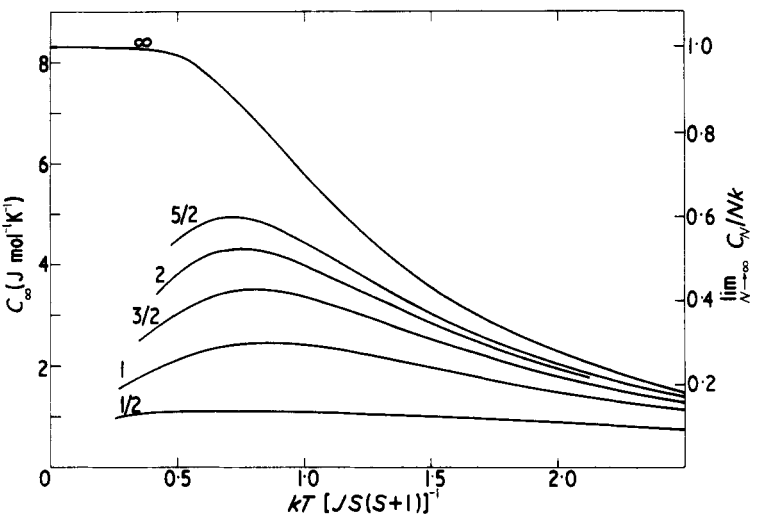

Figure 2. Specific heat of an infinite chain with ferromagnetic interaction ($J > 0$), for different spin. The curves are drawn in the region where the estimated error is less than 4%.

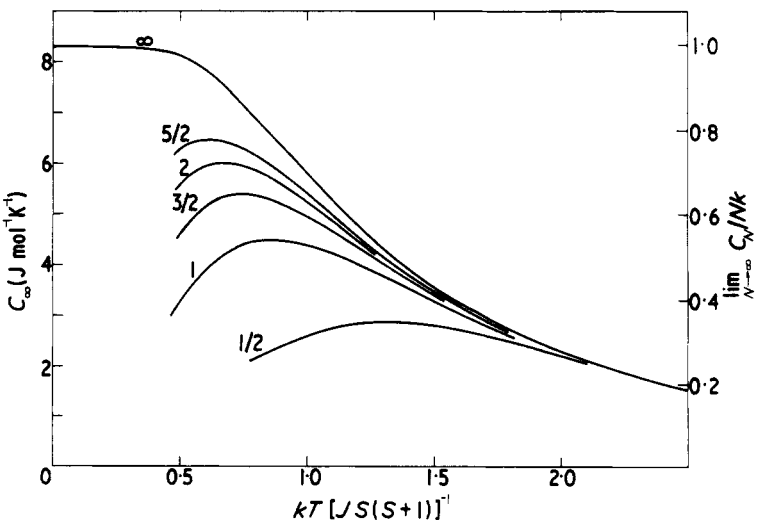

Figure 3. Specific heat of an infinite chain with antiferromagnetic interaction ($J < 0$), for different spin. The curves are drawn in the region where the estimated error is less than 4%.

decreasing with increasing temperature. A value of 0·5% is obtained in all cases in the neighbourhood of T_m, and for higher temperatures the error can be neglected.

The main features of C are as expected. For all S (except $S = \infty$) the ferromagnetic chain has a lower specific heat than the antiferromagnetic arrangement, but the differences gradually diminish with increasing spin. In the classical limit there is no dependence on the sign of J. It is clear that the approximation of the specific heat for $S = \frac{5}{2}$ by the infinite-spin model is rather poor.

Presentation of the results in this form is not very suitable in experimental physics where the curves in general are fitted to data points in order to check for instance the one-dimensional character of the substance and to estimate the magnitude of J. We have therefore attempted to derive a simple expression that represents the curves. For practical applications we have chosen a formula with a few parameters that approximates C close enough to be of experimental use. (Presentation of the exact series and tables of the estimated limit for the complete temperature scale is in progress.)

A suitable formula was found in the expressions obtained from applications of Padé approximants to the HTE of C (Baker 1961):

$$C = \frac{\sum_{i=2}^{M} a_i \beta^i}{(\beta - \beta_0)^\gamma (\beta - \beta_0^*)^\gamma}. \tag{3}$$

The coefficients a_i are normally determined by the requirement that the series expansion of equation (3) results in the original HTE. In this case however, we merely used the coefficients in formula (3) as parameters and calculated their values such that (3) is valid in the sense of a least-squares approximation. Limiting the upper bound in the nominator to four, we performed fits for a variety of temperature intervals. The requirement that the largest difference between the function and the 'true' specific heat does not exceed 2% for $\beta > 0$ (ferromagnet) as well as for $\beta < 0$ (antiferromagnet) determined the appropriate temperature interval. The values of the parameters, together with the temperature range and T_m, are given in table 1. The largest discrepancies are found for the ferromagnetic chain with $S = \frac{1}{2}$, but even in that case the differences are so small that a plot of the two curves is not meaningful for typographic reasons.

Table 1. Review of the values for the parameters in the formula

$$F = \frac{a_2 K^2 + a_3 K^3 + a_4 K^4}{(1 + b_1 K + b_2 K^2)^\gamma}$$

that fit best to the calculated specific heat (C_∞), for different spin ($K = 1/\mathcal{T}$). The columns headed 'interval' indicate the region for $\mathcal{T}$ where the difference between F and C_∞ is less than 2%. $\mathcal{T}_m$ is the reduced temperature for which C_∞ reaches its maximum value.

	Parameters						$J > 0$		$J < 0$	
S	a_2	a_3	a_4	b_1	b_2	γ	interval	$\mathcal{T}_m^*$	interval	$\mathcal{T}_m^*$
$\frac{1}{2}$	10·935	1·6555	2·8722	0·6900	1·7030	2·1765	1·06–4·0	0·88	0·95–4·0	1·32
1	10·745	−0·1034	1·0334	0·2450	0·8502	2·1078	0·59–2·8	0·85	0·56–4·0	0·86
$\frac{3}{2}$	10·939	−0·6760	0·6481	0·1047	0·6514	2·0792	0·50–4·0	0·80	0·50–4·0	0·75
2	11·072	−0·9653	0·4408	0·0408	0·6041	1·9449	0·40–4·0	0·75	0·50–4·0	0·67
$\frac{5}{2}$	11·097	−0·8511	0·1799	0·0195	0·5845	1·8081	0·38–4·0	0·71	0·36–4·0	0·62

It should be noted that no conclusions can be drawn from the gradual change of γ. This parameter is only approximate and by no means an exact result. A detailed study for all temperatures with comparison of results from different techniques is in progress and will be published in due course.

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