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1997 J. Phys.: Condens. Matter 9 6913

(http://iopscience.iop.org/0953-8984/9/32/013)

J. Phys.: Condens. Matter **9** (1997) 6913–6920. Printed in the UK PII: S0953-8984(97)81126-5

Wave-vector-dependent magnetic susceptibility of classical Heisenberg rings

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Received 21 January 1997, in final form 25 April 1997

Abstract. We first extend previous results of G S Joyce so as to derive the exact wave-vector-dependent susceptibility $\chi_N(q, T)$ for a ring of N classical Heisenberg spins with isotropic nearest-neighbour interactions. Our major result however is a simple, highly accurate, analytic approximation for $\chi_N(q, T)$ which nevertheless preserves an associated sum rule over the Brillouin zone.

In recent years there has been renewed interest in one-dimensional models of magnetism with the advent and refinement of the ability to fabricate nanometre-scale magnetic systems [1, 2]. A wide variety of molecular clusters containing relatively small numbers of magnetic ions (e.g. as few as four) can now be fabricated [3, 4] and these provide novel systems in which to test basic theories of magnetism and offer the prospect of new applications. Quite often the magnetic moments in these clusters are positioned in a simple ring shape, as in the 'ferric wheel', which consists of ten Fe^{3+} ions, each with $S = \frac{5}{2}$, bound in a molecular ring structure [4] which interact through the Heisenberg exchange mechanism. Whereas there is a large literature devoted to theory and experiment of one-dimensional magnetic systems in the form of long chains, there are few results for interacting Heisenberg spins on small systems.

The purpose of this article is twofold. First, we derive exact expressions for the wave-vector-dependent susceptibility $\chi_N(q, T)$ for a system of N classical Heisenberg spins with isotropic nearest-neighbour interactions positioned on a ring. The quantity $\chi_N(q, T)$ (defined below in (8)) is required in numerous physical contexts, e.g. in computing time-dependent spin-correlation functions [5] or the NMR spin–lattice relaxation time [6]. (In the following, we will generally simplify our notation by suppressing the temperature variable T and write $\chi_N(q)$.) The relevance of the classical Heisenberg model stems from the fact that elsewhere [7] we have demonstrated for the ferric wheel that a simple approximate treatment of interacting classical Heisenberg spins provides results for the magnetic susceptibility in excellent agreement with experiment except at low temperatures, where quantum effects hold sway. Previously, Fisher [8] and Joyce [9] have investigated the equilibrium properties of the one-dimensional classical Heisenberg model for free and cyclic boundary conditions, respectively. These authors have, for their respective systems, given expressions for the magnetic susceptibility $\chi_N(0)$, which is the $q = 0$ limit of what we seek here. While the expression for the open-chain susceptibility is extremely simple, that for the ring is rather complicated and involves infinite series of modified Bessel functions. We note that

0953-8984/97/326913+08$19.50

$\chi_N(q)$ is the Fourier transform of the equilibrium two-spin correlation function, $C_N(n)$, defined below in (2). Whereas for the open chain the correlation function exhibits simple exponential decay with increasing n, $C_N(n) = \exp(-|n|/\xi)$, independent of the number of spins N in the chain [8], the correlation function for the ring is rather involved, also consisting of infinite series of modified Bessel functions [9]. (Here the correlation length ξ is given by $\xi^{-1} = \ln[|\coth K - K^{-1}|]$, where $K = J/(k_B T)$ is the dimensionless nearest-neighbour coupling constant.) Of course, for large enough N, the nature of the boundary conditions becomes immaterial and the correlation function for the ring takes the form of that for the open chain, i.e. simple exponential decay with increasing n. For a finite ring, however, the correlation function satisfies a cyclic condition, $C_N(n) = C_N(N-n)$. The correlation function for the finite ring therefore *cannot* decay merely as a simple exponential with increasing n. The impact of the cyclic condition is especially great for small rings, with, say, $N = 10$.

The *second* purpose of this article is to present a highly accurate, analytic approximation for $\chi_N(q)$ for a ring of N spins. Computing the exact $\chi_N(q)$ (see (11)) for the ring entails the summation of infinite series of modified Bessel functions. As we will see, these series are such that, for progressively lower temperatures, increasingly more terms must be included in the sum to achieve good accuracy. Besides the tedium of summing large numbers of Bessel functions, computations in the large-argument, large-order regime trigger numerical instabilities unless effective countermeasures are employed. A physically motivated, *approximate* expression for $\chi_N(q)$ for the ring, hopefully as simple as that for the open chain, would therefore be highly desirable. Indeed, we show that, when compared with the exact quantity, equation (16) provides an *excellent* approximation over the entire Brillouin zone of wave vectors for all but extremely low temperatures. Our approximant for $\chi_N(q)$ is based on a physical approximation for the underlying correlation function, $C_N(n)$, given in (15), that combines the expected exponential decay as a function of n for $n \ll N$ with the cyclic condition of the finite system. We also note that our approximation for $\chi_N(q)$ will be seen to preserve an exact sum rule over the Brillouin zone.

In what follows, we briefly review some of the known thermodynamic properties of a ring of classical Heisenberg spins. We then successively derive exact expressions for $\chi_N(q)$, present our approximation for $\chi_N(q)$, and discuss the performance of our approximant.

The classical spin Hamiltonian for a one-dimensional system of N Heisenberg spins with a cyclic boundary condition and isotropic nearest-neighbour interactions originates in the associated quantum-mechanical model Hamiltonian

$$H_S = -J_S \sum_{i=1}^{N} \boldsymbol{S}_i \cdot \boldsymbol{S}_{i+1} - \mu_S \boldsymbol{B} \cdot \sum_{i=1}^{N} \boldsymbol{S}_i \tag{1a}$$

where the $\boldsymbol{S}_i$ are quantum spin operators, with $\boldsymbol{S}_{N+1} \equiv \boldsymbol{S}_1$, J_S is the exchange interaction energy, $\boldsymbol{B}$ is the external magnetic field, and $\mu_S = g\mu_B$ is the magnetic moment per spin, with g the Landé g-factor and μ_B the Bohr magneton. We note that $(J < 0)$ $J > 0$ promotes (anti-) ferromagnetic ordering at low temperature. The classical spin approximation consists of replacing the quantum spin operators with classical vectors of fixed length $\sqrt{S(S+1)}$ that are free to orient in any direction. Rescaling J_S by $J_S \to J = S(S+1)J_S$ and μ_S by $\mu_S \to \mu = \mu_S\sqrt{S(S+1)}$ then leaves a model Hamiltonian

$$H = -J \sum_{i=1}^{N} \hat{\boldsymbol{e}}_i \cdot \hat{\boldsymbol{e}}_{i+1} - \mu \boldsymbol{B} \cdot \sum_{i=1}^{N} \hat{\boldsymbol{e}}_i \tag{1b}$$

defined in terms of classical three-dimensional unit vectors, $\hat{\boldsymbol{e}}_i$, free to point in any direction, with $\hat{\boldsymbol{e}}_{N+1} \equiv \hat{\boldsymbol{e}}_1$. In what follows, we will consider all quantities evaluated in zero magnetic field.

We denote the two-spin correlation function for the N-spin ring as

$$C_N(n) = \langle \hat{e}_i \cdot \hat{e}_{i+n} \rangle_N \equiv Z_N^{-1} \int \mathrm{d}\Gamma \;\; \exp(-\beta H) \hat{e}_i \cdot \hat{e}_{i+n} \tag{2}$$

where $\beta \equiv (k_B T)^{-1}$, $\mathrm{d}\Gamma \equiv \prod_{i=1}^{N} (\mathrm{d}\Omega_i / 4\pi)$, with $\mathrm{d}\Omega_i = \sin\theta_i \; \mathrm{d}\theta_i \; \mathrm{d}\phi_i$ the element of solid angle about $\hat{e}_i$, and where Z_N is the partition function, $Z_N = \int \mathrm{d}\Gamma \;\; \exp(-\beta H)$. The exact value of the latter quantity in zero magnetic field is given by the infinite series [9]

$$Z_N(K) = \sum_{l=0}^{\infty} (2l+1) f_l^N(K) \tag{3}$$

where $K = \beta J$ and $f_l(K) \equiv \sqrt{\pi/(2K)} I_{l+1/2}(K)$ is the modified spherical Bessel function of order l. These functions have the property that $f_l(-K) = (-1)^l f_l(K)$ and they decay extremely rapidly with increasing l for $l > |K|$. Thus, for numerical calculations, the higher the temperature, the fewer the terms of (3) that are required to be summed. For a finite ring with translational symmetry, we shall show that the correlation function has the cyclic property

$$C_N(n) = C_N(N-n). \tag{4}$$

(We note that this condition implies a distinct set of relations among the correlation functions only for $0 \leqslant n \leqslant [N/2]$, where $[N/2]$ is the integer part of $N/2$.) Equation (4) is therefore a boundary condition to be met by any approximate theory of the correlation function.

For zero magnetic field, Joyce [9] has also derived an exact double infinite-series expression for the correlation function in terms of the Wigner $3j$-symbol. Elsewhere [7] we show that his result may be simplified to a single infinite sum, namely

$$C_N(n, K) = Z_N^{-1} \sum_{l=0}^{\infty} (l+1) f_l^N(K) [\rho_l^n(K) + \rho_l^{N-n}(K)] \tag{5}$$

where $\rho_l(K) \equiv f_{l+1}(K)/f_l(K)$. We note that $\rho_l(-K) = -\rho_l(K)$ and that $|\rho_l| < 1$ for all $l \geqslant 1$. It follows at once from (5) that the cyclic property (4) is obeyed. From (5) it can be shown that

$$\operatorname*{Lim}_{N\to\infty} C_N(n, K) = \rho_0^n(K) \equiv u^n(K) \tag{6}$$

where $u(K) = I_{3/2}(K)/I_{1/2}(K) = \coth K - K^{-1}$ is the Langevin function. Thus, the decay of the correlation function is exclusively exponential for the infinite ring. The result in this limiting case is consistent with Fisher's finding [8] that for the open chain of classical Heisenberg spins

$$C_N^{\text{chain}}(n, K) = u^n(K) \tag{7}$$

independently of N. We note that for a ring with N even, $C_N(n, -K) = (-1)^n C_N(n, K)$, whereas for odd N there is no simple relation between the correlation functions for ferro- and antiferromagnetic couplings. We also note that the requirement $C_N(0, K) = 1$ is satisfied by (5).

The zero-field, wave-vector-dependent susceptibility per spin can be written as

$$\chi_N(q, K) = \frac{C}{T} N^{-1} \sum_{n=1}^{N} \sum_{m=1}^{N} \mathrm{e}^{\mathrm{i}q(n-m)} \langle \hat{e}_n \cdot \hat{e}_m \rangle_N \tag{8}$$

where the constant C is given by $C = \mu^2/(3k_B)$. Using the properties of the correlation functions listed above, it can easily be shown that $\chi_N(q, K) = \chi_N(\pi - q, -K)$ for N even.

There is no analogous result for odd N. We note that, for any N, $\chi_N(q)$ obeys the following sum rule:

$$\frac{T}{2\pi C}\int_{-\pi}^{\pi}\chi_N(q, K)\,\mathrm{d}q = C_N(0, K) = 1. \tag{9}$$

Using the cyclic property (4), the definition of $\chi_N(q)$ depends on whether N is even or odd. For N odd we have

$$C^{-1}T\chi_N(q, K) = 1 + 2\sum_{m=1}^{[N/2]}\cos(mq)C_N(m, K) \tag{10a}$$

whereas for N even

$$C^{-1}T\chi_N(q, K) = 1 + 2\left(\sum_{m=1}^{[N/2]-1}\cos(mq)C_N(m, K)\right) + \cos(Nq/2)C_N(N/2, K). \tag{10b}$$

Substituting the exact expression (5) into (10a) and (10b), respectively, we find

$$C^{-1}T\chi_N(q, K) = 1 + 2Z_N^{-1}\sum_{l=0}^{\infty}(l+1)f_l^N \times\left[\frac{\rho_l(\cos q - \rho_l) - \rho_l^N(1 - \rho_l\cos q) + 2\sin(Nq/2)\rho_l^{[N/2]+1}F_l(q)}{1 - 2\rho_l\cos q + \rho_l^2}\right] \tag{11}$$

where

$$F_l(q) = \begin{cases}(1+\rho_l)\sin(q/2) & (N \text{ odd})\\ \sin q & (N \text{ even})\,.\end{cases} \tag{12}$$

By setting $q = 0$, we recover Joyce's result [9]:

$$C^{-1}T\chi_N(0, K) = 1 + 2Z_N^{-1}(K)\sum_{l=0}^{\infty}(l+1)\left[\frac{f_l^N f_{l+1} - f_l f_{l+1}^N}{f_l - f_{l+1}}\right]. \tag{13}$$

Finally, considering the limit $N\to\infty$ in (11), it can be shown that

$$C^{-1}T\chi_\infty(q, K) = \frac{1 - u^2(K)}{1 - 2u(K)\cos q + u^2(K)}. \tag{14}$$

The form of (14) is common to infinite, one-dimensional models with an exponentially decaying correlation function, where the parameter u can be identified in terms of the correlation length, $|u| = \exp(-\xi^{-1})$.

Inspecting (5), one notes that the cyclic property for the correlation function, equation (4), is separately obeyed by each term $\rho_l^n + \rho_l^{N-n}$ of the sum. The cyclic condition, however, would equally well be satisfied by an *approximate* correlation function with the basic form $C_N(n, K) = [v^n(N, K) + v^{N-n}(N, K)]/[1 + v^N(N, K)]$, where $v(N, K)$ is some appropriately chosen, effective function of the coupling strength. Note that this approximant preserves the short-distance requirement $C_N(0, K) = 1$. Without loss of generality we can assume that $|v(N, K)| \leqslant 1$. Since the large-system limit, equation (6), should also be obeyed, we have the restriction that $\mathrm{Lim}_{N\to\infty}\, v(N, K) = u(K)$. Although other choices are possible [7] for the function $v(N, K)$, and in fact provide superior results, the simplest choice is just $v(N, K) = u(K)$, i.e. independent of N. Thus, we adopt as an approximation the simple formula

$$C_N(n, K) \cong [u^n(K) + u^{N-n}(K)]/[1 + u^N(K)]. \tag{15}$$

This approximation combines the expected exponential decay of the correlation function with the cyclic property for the finite system and properly reduces to pure exponential decay in the large-N limit. Elsewhere [7] we have shown that if $N \geqslant 6$, equation (15) provides an accurate approximation to (5) at least for $|K| < 3$, i.e. excluding very low temperatures. It should be remarked that for low temperature, the classical Heisenberg Hamiltonian given by (1b) cannot adequately represent the quantum-mechanical counterpart given by (1a).

Substituting (15) into (10a) and (10b) leads to the following approximate result for $\chi_N(q)$:

$$\chi_N^{\text{approx}}(q, K) \cong \left(\frac{1-u^N}{1+u^N}\right)\chi_\infty(q, K) + \frac{C}{T}\frac{4\sin(Nq/2)u^{[N/2]+1}F(q, K)}{(1+u^N)(1-2u\cos q+u^2)} \tag{16}$$

where

$$F(q, K) = \begin{cases} (1+u)\sin(q/2) & (N \text{ odd}) \\ \sin q & (N \text{ even}) \end{cases} \tag{17}$$

and where $\chi_\infty(q, K)$ is given by (14).

For completeness, we also obtain $\chi_N(q)$ for the open chain. By substituting (7) into (8), we obtain

$$C^{-1}T\chi_N^{\text{chain}}(q, K) = \frac{1-u^2}{1-2u\cos q+u^2} - \frac{2u}{N(1-2u\cos q+u^2)^2} \times \{(\cos q(1+u^2)-2u)(1-u^N\cos(Nq)) + u^N\sin(Nq)\sin q(1-u^2)\}. \tag{18}$$

Note that there are no even–odd effects in (18). It is easy to see that by letting $N \to \infty$ in (18), we recover (14), as we should. Setting $q = 0$ in (18), we recover Fisher's result [8]:

$$C^{-1}T\chi_N^{\text{chain}}(0, K) = \frac{1+u}{1-u} - \frac{2u(1-u^N)}{N(1-u)^2}. \tag{19}$$

We have now derived three expressions for $\chi_N(q)$ for a one-dimensional system of N classical Heisenberg spins: equation (18), which is the exact result for the finite open chain; equation (11), the exact result for the finite ring; and equation (16), an approximate result for the finite ring. We note that each of these expressions satisfies the sum rule given in (9). The fact that the approximate result for the ring, equation (16), satisfies the sum rule can be traced to the fact that our approximation, equation (15), for the correlation function preserves the property $C_N(0, K) = 1$.

In figure 1 we plot $(3|J|/\mu^2)\chi_N(q)$ versus q for a system with $N = 6$ and $K = 2$, for each of the three expressions, equations (11), (16) and (18). To compute the exact results, we have used the following method to efficiently and accurately evaluate the necessary modified spherical Bessel functions, $f_l(K)$. We use the recurrence relation for the functions $f_l(K)$ (equation (10.2.18) of reference [10]) to obtain values of the ratios $\rho_l(K) = f_{l+1}(K)/f_l(K)$. To avoid crippling numerical instabilities, it is necessary to invoke a backward iteration method [11] to evaluate $\rho_l(K)$. One then has $f_l = f_0\rho_0\rho_1\cdots\rho_{l-1}$, where f_0 has the simple form $f_0(K) = \sinh(K)/K$.

It can be seen in figure 1, for this temperature ($K = 2$), that (16) provides an excellent approximation when compared with the exact results. We note, however, that the approximation rapidly improves for increasing values of N. In figure 2, we show the same quantities as for figure 1, except that $N = 10$. In this case one cannot distinguish between the exact and approximate results for the ring. In general, the approximate result given by (16) is quite robust. This is illustrated in figure 3, where we show $(3|J|/\mu^2)\chi_N(q)$

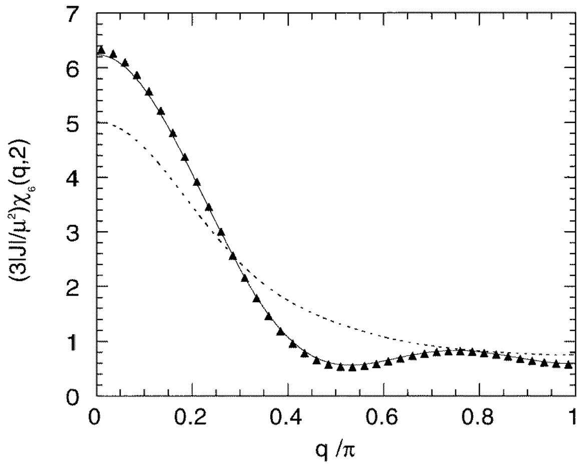

Figure 1. The magnetic susceptibility $\chi_N(q)$ as a function of the wave vector q for a system of $N = 6$ interacting classical Heisenberg spins for $K = 2$: ring, exact (equation (11)), solid curve; ring, approximate (equation (16)), solid triangles; open chain (equation (18)), dashed curve.

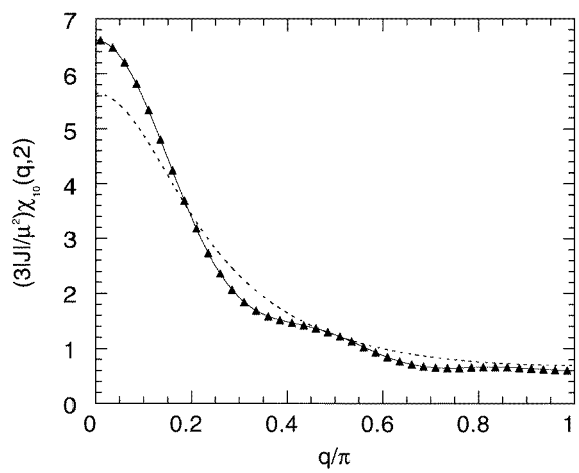

Figure 2. The magnetic susceptibility $\chi_N(q)$ as a function of the wave vector q for a system of $N = 10$ classical Heisenberg spins for $K = 2$ (the key is the same as for figure 1).

for the ten-spin ring with $K = 20$. It can be seen that while the quantitative agreement with the exact result has degraded, the qualitative agreement is excellent despite the low value of the temperature. We note that the performance of the open-chain formula, equation (18), is considerably inferior.

The oscillations seen in figure 3 for the exact and approximate ring results arise from what can be called the 'even–odd' terms in (11) and (16), respectively, the terms proportional to $\sin(Nq/2)$. With increasing N, there will be a decreased period of oscillation in the behaviour of $\chi_N(q)$ versus q. The amplitude of the oscillations, however, is temperature dependent and decreases exponentially with increasing temperature. For increasing N, therefore, there will be significant oscillations in $\chi_N(q)$ only for progressively smaller temperatures, until in the limit $N \to \infty$, $\chi_N(q)$ is purely monotonic for all temperatures.

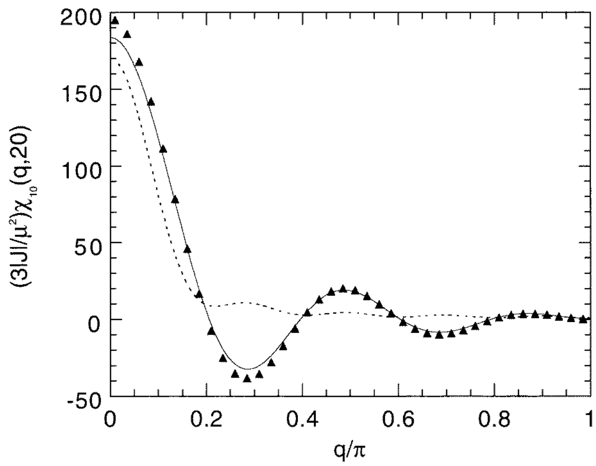

Figure 3. The magnetic susceptibility $\chi_N(q)$ as a function of the wave vector q for a system of $N = 10$ classical Heisenberg spins for $K = 20$ (the key is the same as for figure 1).

The fact that $\chi_N(q)$ becomes negative for selected q-intervals (as occurs in figure 3), and hence that the magnetization would be directed oppositely to that of a wave-vector-dependent magnetic field, would appear to be restricted to the small-N, low-temperature regime.

In summary, we have derived the exact wave-vector-dependent susceptibility $\chi_N(q)$ for a one-dimensional system of classical Heisenberg spins with isotropic nearest-neighbour interactions for both a closed ring and an open chain, equations (11) and (18), respectively. In the case of the ring, the exact results entail the summation of infinite series of modified spherical Bessel functions. In contrast, the simple formula given by (16) provides excellent approximate results when compared with the exact quantity. Equation (16) is based on the approximate formula (15) for the two-spin correlation function. This simple approximation combines the expected exponential decay of the correlation function with the cyclic property, equation (4), associated with the finite ring. Furthermore, the approximate $\chi_N(q)$ based on this approximation for the correlation function satisfies the exact sum rule given by (9). Elsewhere [12], we use the present approximate result for $\chi_N(q)$ to derive a theoretical expression for the NMR spin–lattice relaxation time of small rings. In that work, the predictions of our theory are compared to experimental data for ring structures with $N = 6, 10$.

Acknowledgment

Ames Laboratory is operated for the US Department of Energy by Iowa State University under contract W-7405-Eng-82.

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