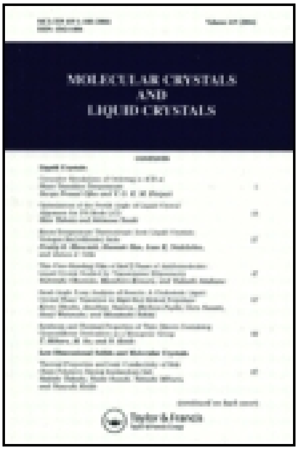

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Monte Carlo Simulation: a Simple Tool to Derive the Thermodynamic Properties of Polynuclear Magnetic Systems

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The simulation of the magnetic properties of S=5/2 extended 1D, 2D and 3D networks using MonteCarlo method (MC) is presented in this paper. It is shown that the MC method gives better results at low temperature than the others approximate methods for simple systems with an unique interaction between the magnetic ions. The case of alternating chains and honeycomb networks with two different J values have been also treated. The J values obtained by MC simulation for alternating chains are comparable with those derived from Drillon's law. For the honeycomb networks, the J values found by the MC approach are in good agreement with the values found for dinuclear complexes with the same bridges.

Keywords: Monte-Carlo simulation; alternating chains; honeycomb network

INTRODUCTION

The quest for molecular based magnets[1-3] and high-spin molecules[4-6], and more generally the molecular crystal engineering, has led to the synthesis of esthetic extended networks[7] and high nuclearity spin clusters[8]. Unfortunately, the huge (or infinite) number of possible configurations in these systems makes it impossible to calculate the exact partition function, and consequently the derivation of the thermodynamic properties (magnetic

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susceptibility, specific heats, etc). Till now for extended networks nobody has been able to go beyond the 2D Ising model for the calculation of the exact partition function. As for magnetic clusters, the present limit seems to be around 8 spins S=5/2 if the diagonalisation procedure is used. This is since long a well-known problem. In order to tackle this problem physicists have developed approximate methods such as high temperature expansion of the partition function[9], closed chain computational procedure[10, 11] or density matrix renormalization group approach (DMRG)[12, 13]. Nevertheless all these approaches are either of limited applicability (DMRG) or difficult to implement (high temperature expansion). Among all these approximate methods, Monte-Carlo simulation[9] seems to be the only one gifted with a wide range of applicability. Moreover this method is relatively simple to use in the case of classical spin approach.

We wish to report here our first results using the Monte-Carlo method and more precisely on the Metropolis algorithm to derive the thermodynamic properties of extended 1D, 2D and 3D systems with spins S=5/2. In one, we have tested the reliability of the Monte-Carlo method on regular networks for which alternative procedures exist. Secondly we have simulated the magnetic properties of original 1D and 2D systems with one or two different interactions between the magnetic ions.

MONTE-CARLO METHOD

A classical problem in statistical physics is to compute average quantities of macroscopic observables such as magnetization M for a magnetic system.

$$\langle M \rangle = \frac{\sum_{i=1}^{\infty} M_i e^{-E_i/kT}}{\sum_{i=1}^{\infty} e^{-E_i/kT}} \qquad (1)$$

As mentioned before, it is generally not possible to compute exactly this quantity (1) due to the infinite number of configurations. The basic idea of Monte-Carlo calculation is to approximate equation (1) where the sum run over all states by a partial sum on a subset of characteristic configurations

$$\langle M\rangle = \frac{\sum_{i=1}^{N} M_i e^{-E_i/kT}}{\sum_{i=1}^{N} e^{-E_i/kT}} \tag{2}$$

In the limit of N →∞ formula (2) is identical to (1).

One possibility is to choose randomly the configurations for the subset. But due to the rapidly varying exponential function in the Boltzmann distribution, most of the chosen configurations will bring a negligible contribution to the sum in formula (2) since E_i will be relatively large. The ideal situation would be then to sample the configurations with a probability given by their Boltzmann weight. This point is illustrated in Figure 1 for a fictitious system with 20 levels equally spaced by 1K. In this example two samples of 40 states have been generated, one randomly and the other one following the Boltzmann distribution for T=10K. This plot clearly shows that the high energy states are predominant in the random sample when compared to the ideal Boltzmann distribution and will bias the calculation of the average quantities.

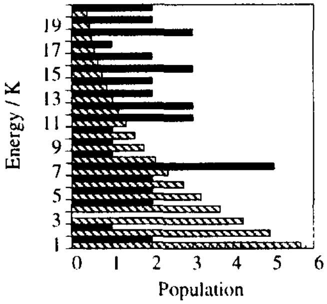


Figure 1 : random sample of 40 states in black, sample of 40 states following the Boltzmann distribution in hatched

For instance, the calculated average energy of the random sample is 7.9 K which a poor approximation to the average energy <E> being 6.3 K for such a system.

Practically, how is it possible to generate a sample of configurations following the Boltzmann distribution ? If we consider a network of Ising spin, we start from a given spin configuration as it is shown in Figure 2 and we try to flip one spin of the network at each Monte Carlo loop.

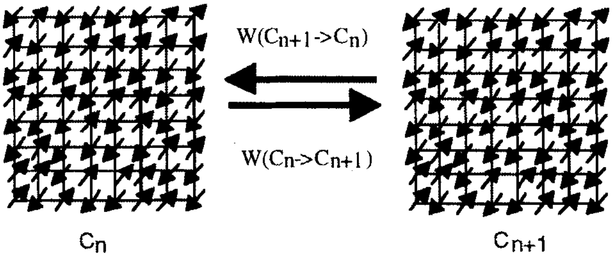


Figure 2

Hence we need to know is the probability of the transition $W(C_n \text{->} C_{n+1})$ from the spin configuration C_n to the spin configuration at the iteration n+1. After several iterations (thermalization process) the transition probability must be independent of the "computer time" (the number of iteration) and should depend on the energy difference between the two configurations C_n and C_{n+1}. One way to fulfil this requirement is to respect the so-called detailed balance condition which is written as formula (3) for a of Boltzmann distribution.

$$\frac{W(C_n->C_{n+1})}{W(C_{n+1}->C_n)}=\frac{p(C_{n+1})}{p(C_n)}=\frac{e^{-E_{C_{n+1}}/kT}}{e^{-E_{C_n}/kT}} \tag{3}$$

This condition gives a relation between the ratio of transition probabilities and the ratio of configurations probabilities. It is worthy to note that equation (3) is independent of the partition function Z and that all the quantities in the last part of (3) are known or can be calculated in the case of classical model. The next step is to give arbitrary values to $W(C_n\text{->} C_{n+1})$ and $W(C_{n+1}\text{->} C_n)$ respecting the detailed balance condition. In 1953, Metropolis, Teller and Rosenbluth proposed the following choice for W[14]

$$\begin{aligned} W(C_n->C_{n+1}) &= e^{-\Delta E/kT} && if\, \Delta E>0 \\ &= 1 && if\, \Delta E\leq 0 \\ with\, \Delta E = E_{C_{n+1}} - E_{C_n} \end{aligned} \tag{4}$$

This choice satisfies the detailed balance condition and allows to sample the configurations according to the Boltzmann distribution. The last but not least step of a Monte-Carlo simulation is to define whether the spin flip is accepted or not. According to the Metropolis algorithm this condition is not precise but only the probability of the transition to the new configuration is given. The approbation of the transition is tuned by comparison with a real random number r in the [0,1] range according to the following rule.

$$\text{if } W(C_{n+1} \text{->} C_n) > r\,[0,1] \text{ the spin flip is accepted} \qquad (5)$$

Following all these steps we are able to generate a sample of representative configurations at a given temperature and thereby to calculate average quantities. Monte-Carlo simulation using the Metropolis algorithm is of great simplicity and easy to program, the core of the program being about ten lines or so. Nevertheless, many points are delicate and can lead to unreliable results.

The principal points to check before obtaining a solid simulation are the thermalization process (number of iteration before generation of the sample), size of the model, number of MC iterations , speed for the decrease of temperature etc...[15].

II REGULAR S=5/2 SYSTEMS

In order to test the reliability of the MC method in molecular magnetism we have applied this approach on well documented S=5/2 regular systems such as 1D chains, 2D square and honeycomb lattices and cubic 3D network. For all these nets, there are alternative approximate methods to derive the thermodynamic properties which allow comparison with the MC results. These simulations were realized with the Heisenberg model. The interaction energy between two magnetic centers is calculated according to eq (6).

$$E = -J\,\sqrt{S_1(S_1+1)}\,.\,\sqrt{S_2(S_2+1)}\,\cos\theta_{\vec{S_1}.\vec{S_2}} \qquad (6)$$

The size of the model were equal to 200, 16x16 and 16x16x16 for 1D, 2D and 3D networks respectively. The results are depicted in Figure 3 and compared with those obtained with high temperature expansion of the partition function (HTEPF) except for 1D chain where we plotted the Fischer's law[16].

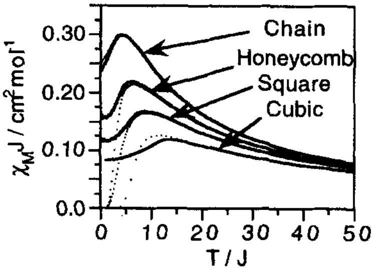


Figure 3 : $\chi_M J$ versus T/J plots obtained by MC simulation (lines), Fisher's law for chain and high temperature series for 2D and 3D network (points).

Before the maximum of $\chi_M J$ plot, the agreement between the MC simulation and the others approaches is excellent. However for the 3D networks, both MC simulation and HTEPF do not present the maximum at the same T/J value. Below the maximum of $\chi_M J$, there is a discrepancy between the MC simulation and the others approaches. The expected behaviour for these kind of infinite systems where there is no gap between the ground state and the first excited states is to reach a finite value for χ at low temperature. Only the Fisher's law and the MC simulation follow this property whereas HTEPF fails to reproduce this behaviour.

For each kind of network we have also tested the MC approach to fit the magnetic data of real systems. In Figure 4 is depicted. the result for $[(N(CH_3)_4][Mn(N_3)]$ compound which crystallizes in a regular cubic network[17].

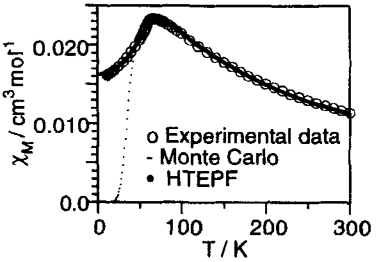


Figure 4 : χ_M versus T/J plots for $[(N(CH_3)_4][Mn(N_3)]$

The magnetic behavior can be reproduced using the interaction parameter J= -5.2 cm^{1} and g= 2.025. These values are close to those find with the HTEPF method (J= 5.cm^{1}) thus enhancing the reliability to the MC results. It is worthy to note that the agreement between the MC simulation and the experimental points is astonishingly good even at low temperature for the 3D system confirming the classical behaviour of S=5/2 spins.

ALTERNATING S= 5/2 CHAINS

We have studied alternating S = 5/2 chains with two different J values between the magnetic ions. The three possible topologies for the interaction have been considered, that is AF-AF, AF-F and F-F where AF and F stand for antiferromagnetic and ferromagnetic respectively. In order to fit the magnetic data of real systems we have proceeded in two steps for each topology of interaction. First, several simulations with different α values in the [0,1] range have been performed, α being the alternating parameter and equals to the ratio J / J'. The results for the AF-AF case are shown in Figure 5 in the form of the $\chi_M J$ versus β=T/J plot .

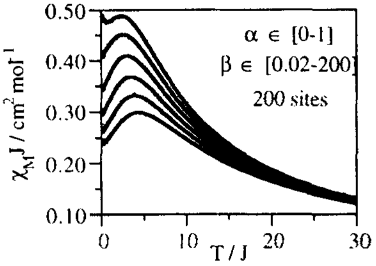


Figure 5

All these plots define a 2D surface depending on β and α. This 2D surface can be fitted with an empirical law as follows.

$$\chi J = \frac{g^2}{4}\,\frac{a_1+a_2\alpha+a_3\alpha^2+a_4\alpha^3+a_5\beta+a_6\alpha\beta+a_7\alpha^2\beta+a_8\beta^2+a_9\alpha\beta^2+a_{10}\alpha^2\beta^2+a_{11}\beta^3+a_{12}\alpha\beta^3+a_{13}\beta^4}{1+b_1\beta+b_2\alpha\beta+b_3\alpha^2\beta+b_4\beta^2+b_5\alpha\beta^2+b_6\alpha^2\beta^2+b_7\beta^3+b_8\alpha\beta^3+b_9\beta^4+b_{10}\beta^5}$$

The fit of the experimental data with this empirical law allows us to determine the J and α values. The results for an AF-AF and a F-AF alternating chains are shown in Figure 6 and Figure 7 together with the fits obtained with the law derived by Drillon et al for classical spin alternating chains[18].

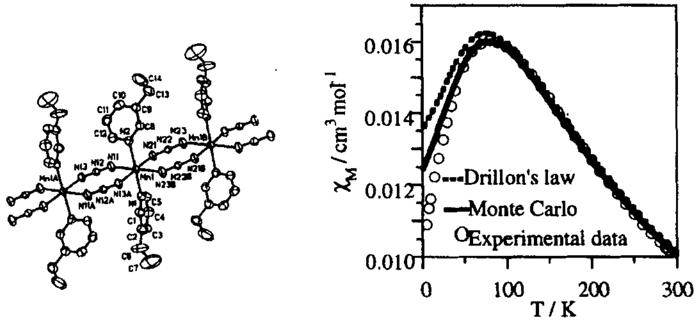


Figure 6 : Crystal structure and magnetic properties of $[Mn(2\text{-}pyOH)_2(N_3)_2]_n$.[19] (a) circles experimental data, solid line Monte-Carlo simulation and dashed line Drillon's law.

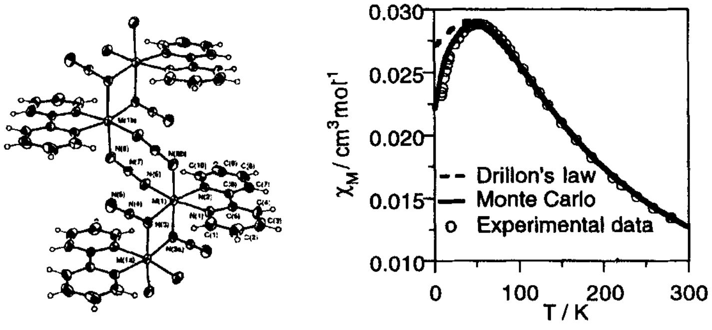


Figure 7 : Crystal structure and magnetic properties of $[Mn(bipy)(N_3)_2]_n$.[20, 21] (a) circles experimental data, solid line Monte-Carlo simulation and dashed line Drillon's law.

In both cases, the agreement found with our empirical laws are better at low temperature than Drillon's law. The results of the best parameters found for the fitting of the magnetic data with MC approach and Drillon'law for both compounds are gathered in Table I.

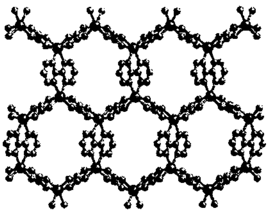
Compound	Method	g	J_1 / cm^{-1}	J_2 / cm^{-1}
$[Mn(2\text{-}pyOH)_2(N_3)_2]_n$.	MC Drillon	2.04 2.03	-13.2 -13.8	-12.3 -11.7
$[Mn(bipy)(N_3)_2]_n$	MC Drillon	1.98 1.99	-12.9 -12.9	+4.9 +5.0

Table I

The parameters found by MC simulation and the Drillon's law are very close in both cases. At this point, we esteem that the interactions parameters extracted from the empirical laws derived from the MC simulation are highly reliable.

HONEYCOMB ALTERNATING NETWORKS

The last example presented in this paper deals with alternating honeycomb networks. In this case, no alternative method has been published yet. As for alternating chains, we have derived empirical laws depending on α=J/J' and β=T/J for the different possible topologies of the interaction in the honeycomb network. These laws have been obtained after several MC simulations with different α values. Using these empirical laws we have fitted experimental data and the results for $[Mn(ox)_2(bpm)]_n$[22] an AF-AF honeycomb network and $[Mn(N_3)_2(bpm)]_n$ [23]a F-AF honeycomb network are presented in Figure 8 and 9 respectively.



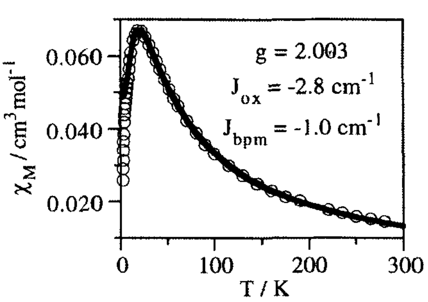


Figure 8: Crystal structure and magnetic properties of $[Mn(bipm)(ox)]_n$, circles experimental data, solid line Monte-Carlo simulation.

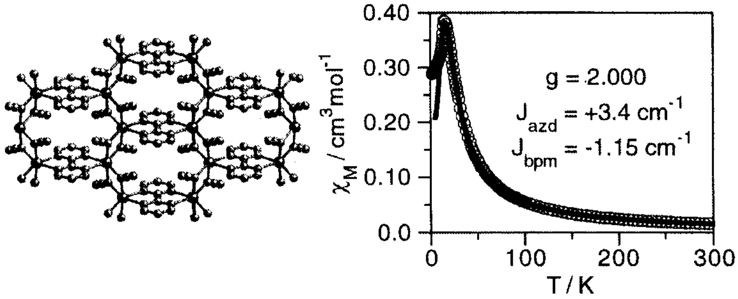


Figure 9 : Crystal structure and magnetic properties of $[Mn(bipm)(N_3)_2]_n$, circles experimental data, solid line Monte-Carlo simulation.

For these two examples the agreement with the experimental data are excellent except at low temperature where there is a discrepancy. Furthermore the values found for the interaction parameters are physically correct. The J values found for the interaction through the oxalato, bipyrimidine or azido bridge are similar to those found in dinuclear or oligomer complexes with the same bridges[22, 24]. We are currently trying to introduce interplanar interaction in order to fit the magnetic data even at low temperature.

CONCLUSION

In this paper we have shown that MC simulation is well adapted to interpret magnetic data of extended networks. The reliability of this method is excellent when compared to other approaches based on different hypotheses. In general MC calculations give a better fit in the low temperature region. In the case where no alternative method exists, MC results are in good accord with those found in discrete systems containing the same corresponding bridges.

Moreover, the MC approach allows to treat original extended systems including 3D networks with several different interactions, for which other methods seem impossible. In contrast to other approximate methods that can only be used by theoretical chemists or physicists, MC simulations can be used by a large audience of magnetochemists.

Nevertheless MC simulation with classical spin presents a severe limitation: only systems with spin ≥ 2 can be treated. To overcome this problem we are on our way to simulate the magnetic properties of high nuclearity spin clusters and extended networks containing quantum spins (S<2) using quantum Monte Carlo method.

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