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Monte Carlo entropic sampling applied to spin crossover solids: the squareness of the thermal hysteresis loop

Jorge Linares [a,*], Cristian Enachescu [a,b], Kamel Boukheddaden [a], François Varret [a]

[a] *Laboratoire de Magnétisme et d'Optique, CNRS-UMR 8634, Université de Versailles St. Quentin-en-Yvelines, 78035 Versailles Cedex, France*
[b] *Faculty of Physics, 'Alexandru Ioan Cuza' University, Bdul Carol I, nr. 11, Iasi, 6600, Romania*

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Abstract

The Monte Carlo entropic sampling method previously presented in [I. Shteto, J. Linares, F. Varret, Phys. Rev. E 56 (1997) 5128] is adapted here to an Ising-like system with short- and long-range interactions. Such model is suited to spin crossover solids [J. Linares, H. Spiering, F. Varret, Eur. J. Phys. B 10 (1999) 271; K. Boukheddaden, J. Linares, H. Spiering, F. Varret, Eur. Phys. J. B 15 (2000) 317] where the long interaction is due to elastic coupling mediated by the lattice, while the short-range interaction originates from the bonding between the spin crossover units [J. Linares, H. Spiering, F. Varret, Eur. J. Phys. B 10 (1999) 271]. Taking into account the different degeneracies g_{HS} for high-spin (HS) and g_{LS} for low-spin (LS) states, the Ising Hamiltonian associated with fictitious spins is written:

$$H = -h\sum \sigma_i - J\sum \sigma_i\sigma_j$$

with

$$h = -\frac{\Delta}{2} + \frac{k_B T \ln(g_{HS}/g_{LS})}{2} + G\langle\sigma\rangle$$

where J and G are the short- and long-range interactions, respectively, and Δ the energy gap of ligand field such that the LS state is the ground state. The numerical method has been tested successfully by comparison to the exact solution for a 1D system: $[Fe(Htrz)_2(trz)](BF_4)_2$ [J. Linares, H. Spiering, F. Varret, Eur. J. Phys. B 10 (1999) 271; J. Krober, J.P. Audière, R. Claude, O. Kahn, J. Hassnoot, F. Grolière, C. Jay, A. Bousseksou, J. Linares, F. Varret, A. Gonthier-Vassal, Chem. Mater. 6 (1994) 1404]. We describe here the results obtained for 2D systems, and show that the squareness of the thermal hystersis loop, associated with the spin-transition, can be correlated to the strength of short-range interactions.

Keywords: Monte Carlo entropic sampling technique; Spin-transition; Thermal hysteresis loop; Ising-like Hamiltonian

1. Introduction

Spin crossover phenomenon continues to attract considerable interest [5–7]. To explain the various thermal behaviours, theoretical models taking into account short- and long-range interactions have been recently proposed [2,3]. In collaboration with Spiering we obtained the analytical solution for a 1D-spin crossover system [2] and we elucidated the origin of the well marked turning points in the thermal hysteresis loops. We later developed a dynamic 1D model, providing analytical expression for the shape of the relaxation curve [3].

For 2D- and 3D-systems the static models have been solved by mean field approach [8,9] or by Bethe approximation [10]. In this work we propose a simple method to solve the Ising-like Hamiltonian, based on the Monte Carlo entropic sampling technique, and including both short- and long-range interactions. The technique is tested here for 1D systems, by comparison to the exact solution, and then applied, for simplicity, to 2D systems.

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* Corresponding author. Fax: +33-139-25-4652.
E-mail address: jlinares@physique.uvsq.fr (J. Linares).

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The report is organised as follows: in the next section we recall the Ising-like model proposed for spin crossover solids. The Monte Carlo entropic sampling is presented in Section 3. In Section 4 we propose a method to solve the Ising-like Hamiltonian using the density of the states $d(m, s)$ obtained by Monte Carlo entropic sampling. This technique is applied for a finite-size (till about 1000 molecules) and for any type of dimension. We analyze the results obtained for 2D systems in terms of balance between short- and long-range interactions.

2. Spin crossover compounds and Ising-like model

Some molecular complexes containing $3d^4$–$3d^7$ metal ions in octahedral symmetry have a high-spin (HS) state with a degeneracy g_{HS} or a low-spin (LS) ground state with degeneracy g_{LS} according to the ligand field strength [5–7]. There are some compounds in which either HS or LS states can be obtained by variation of temperature, pressure, magnetic field or by light irradiation [5–7,11–15]. These compounds called spin crossover or spin-transition systems are textbook examples for molecular bistability at the microscopic and macroscopic scales.

From the theoretical point of view the previous two molecular states HS and LS are generally represented by an Ising fictitious spin σ [2,3,9] with the eigenstates $+1$ (HS) and -1 (LS) having degeneracies g_{HS} and g_{LS}, respectively.

The Hamiltonian including long- (G) and short-range (J) interactions, writes

$$H = -h\sum \sigma_i - J\sum \sigma_i\sigma_j \tag{1}$$

with

$$h = -\frac{\Delta}{2} + \frac{k_B T \ln(g_{HS}/g_{LS})}{2} + G\langle\sigma\rangle \tag{2}$$

where $\Delta > 0$ is the energy gap of ligand field such that the LS state is the ground state.

The fraction of molecules in the HS state (HS fraction) is expressed as $n_{HS} = (1+\langle\sigma\rangle)/2$.

The Hamiltonian expressed by Eqs. (1) and (2) is a true Ising Hamiltonian (not Ising-like), due to the temperature-dependent fictitious field, h, with accounts for the degeneracy ratio.

This Hamiltonian has a exact solution for 1D systems, however, due to the presence of h there are no exact solutions for 2D- or 3D- systems. Mean field approximation [8,9] as well as Bethe approximations [10] and Monte Carlo Metropolis [16] have been used in these cases.

3. Monte Carlo entropic sampling (after Refs. [1,17])

The total energy of the system, derived from the Hamiltonian expression (Eqs. (1) and (2)), writes as a function of two macroscopic variables, as follows:

$$E(m,s) = -hm - Js$$

with

$$m = \sum_{i=1,N} \sigma_i \text{ and } s = \sum_{\langle i,j\rangle} \sigma_i\sigma_j$$

Shteto et al. [1] have described how the biased Monte Carlo sampling method, called entropic sampling, is used to calculate the restricted density of states $d(m, s)$: the number of configurations for a given set of values of m and s. $d(m, s)$ is actually the degeneracy of the macrostate (m,s). The method is briefly recalled here. The entropic sampling method relies on the idea that any desired distribution P, can be derived from a suited Monte Carlo procedure, just by introducing the same distribution as a bias in the detailed balance equation.

$$P_i W(i \to j) = P_j W(j \to i) \tag{3}$$

To explore the entire state space, the suited biased method has to favor configurations belonging to weakly degenerate macrostates (small density of states), and to dampen those belonging to the highly degenerate macrostates (large density of states). The biasing probability, which is best suited for sampling the restricted density of states merely is the inverse of the desired restricted density of states.

$$P_i \propto \frac{1}{d(m_i, s_i)} \tag{4}$$

It follows:

$$\frac{W(i \to j)}{W(j \to i)} = \frac{P_j}{P_i} = \frac{d(m_j, s_j)}{d(m_i, s_i)} \tag{5}$$

where $d(m, s)$ is a priori unknown. Shteto et al. [1] have suggested an interactive method, initiated by the rescaled results of the similar system at smaller size, eventually obtained by a straightforward computation. We term $d_i(m, s)$ the density of states obtained after iteration i. Then, using $d_i(m, s)$ as a bias, a MC sampling is run; it is termed a ‘Monte Carlo stage’ and yields a histogram of the frequency of the macrostates: $H_i(m, s)$.

$$H_i(m,s) \propto d(m,s)\frac{1}{d_i(m,s)} \tag{6}$$

Once corrected for the bias, the resulting restricted density of states is obtained as:

$$d_{i+1}(m,s) \propto d_i(m,s)H_i(m,s) \tag{7}$$

The method is used iteratively: the flatness of the

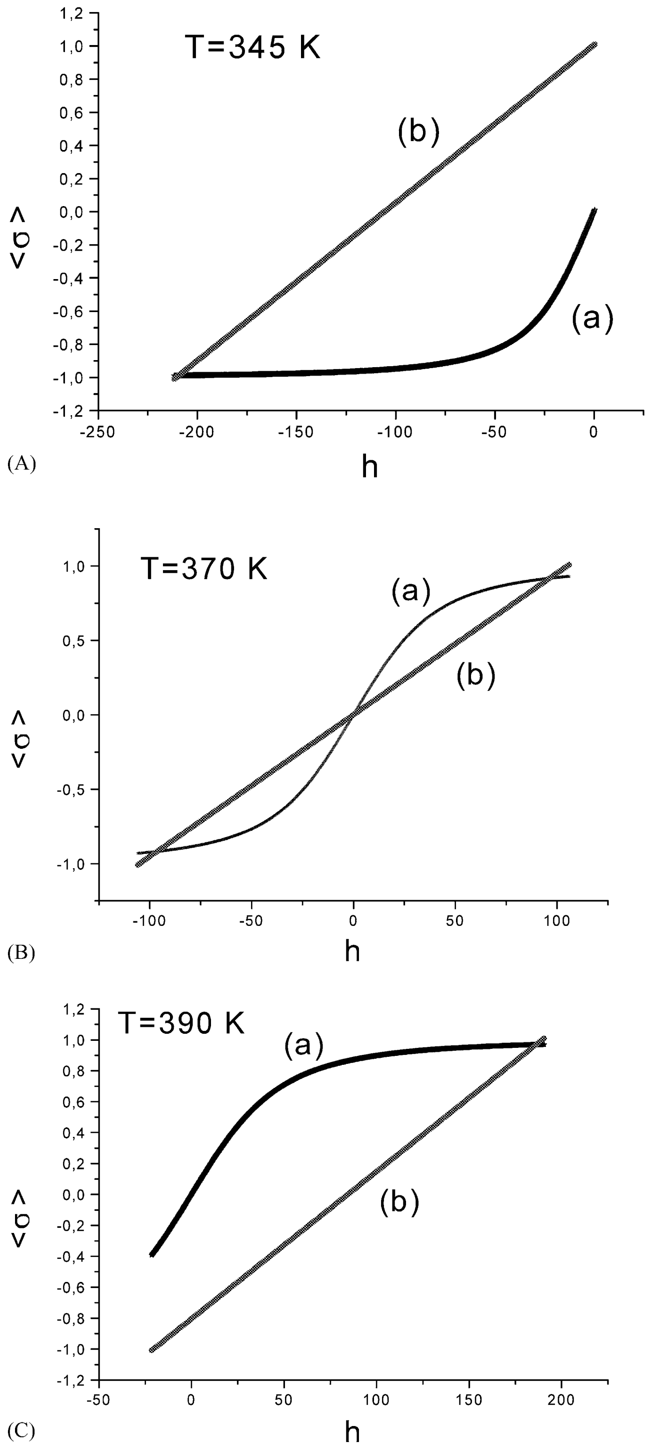

Fig. 1. Fictitious magnetisation $\langle \sigma(h) \rangle$, for a 1D system (100 molecules) using Eq. (8) for $\langle \sigma_a(h) \rangle$ (curve (a)) and Eq. (9) for $\langle \sigma_b(h) \rangle$ for $T = 345$ K (Fig. 1(A)), 370 K (Fig. 1(B)) and 390 K (Fig. 1(C)). The parameter values are: $\Delta = 3126$ K, $\ln(g_{HS}/g_{LS}) = 8.45$ and $J = 400$ K.

histogram $H(m, s)$ is a convenient convergence criterion.

The major advantage of the method is in terms of saving computing time, i.e., of increasing the model size. Indeed, for a system of given size and topology, the entropic sampling has to be performed only once, allowing to fill up the $d(m, s)$ table. Then, for any set of parameter values (temperature, interactions, energy gap, degeneracies), the partition function $Z = \Sigma_{m,s} d(m,s) \exp(-\beta(-hm - Js))$ and all the thermodynamic properties of the system ($\langle \sigma \rangle$, heat capacity, magnetic susceptibility, etc.) can be derived analytically.

4. Model, calculations and discussion

Here we describe the method adapted from 'molecular-field technique' for solving the Ising-like Hamiltonian of a system with N molecules, for which the density of states $d(m, s)$ is provided.

As it is shown in Eqs. (1) and (2) of Section 2, h in the Ising-like Hamiltonian, is function of $\langle \sigma \rangle$, so a straightforward calculation of $\langle \sigma \rangle$ is not possible. We consider a self-consistent technique based on two different expressions of $\langle \sigma(h) \rangle$.

From canonical statistics, a first expression is obtained:

$$\langle \sigma_{\mathrm{a}}(h) \rangle = \frac{\sum_{i=1,M} \frac{m_i}{N} d(m_i, s_i) \exp(-\beta(-hm_i - Js_i))}{\sum_{i=1,M} d(m_i, s_i) \exp(-\beta(-hm_i - Js_i))} \qquad (8)$$

Curves (a) in Fig. 1(A–C) show $\langle \sigma_a(h) \rangle$ calculated for $T = 345$, 370 and 390 K, respectively, for a 1D system (100 molecules with periodic conditions) and for a set values given in the figure caption.

A second expression is derived from the definition of h (Eq. (2)):

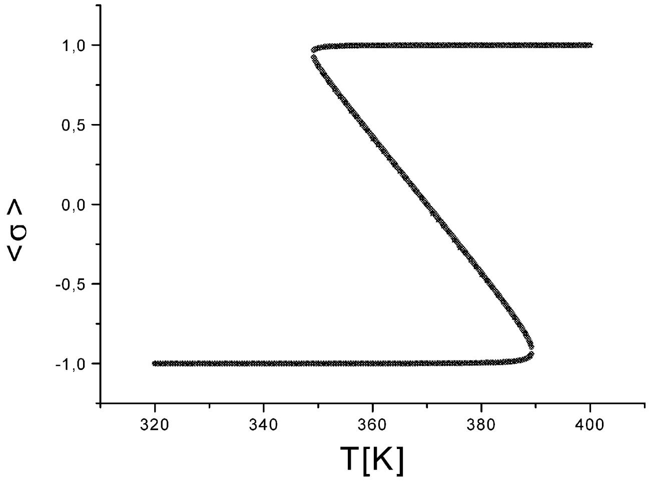

Fig. 2. Fictitious magnetisation $\langle \sigma \rangle$ versus temperature, for a 1D system (100 molecules) using the density of states $d(m, s)$ (*) and by matrix transfer technique (full line). The parameter values are: $\Delta = 3126$ K, $\ln(g_{HS}/g_{LS}) = 8.45$ and $J = 800$ K.

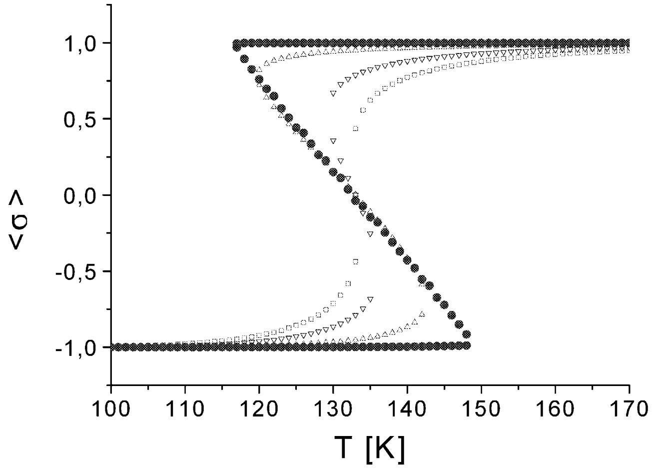

Fig. 3. Fictitious magnetisation $\langle\sigma\rangle$ versus temperature, for a 2D system (64 molecules with periodic conditions). The parameter values are: $\Delta = 1145$ K, $\ln(g_{HS}/g_{LS}) = 9.22$. The short-range interactions are $J = 10$ (square symbols), 20 (down-triangle), 40 (up-triangle) and 100 K (closed circle). The larger J, the wider the hysteresis loop, with increasing squareness.

$$\langle\sigma_b(h)\rangle = \frac{h}{G} + \frac{\dfrac{\Delta}{2} - \dfrac{k_B T \ln(g_{HS}/g_{LS})}{2}}{G} \tag{9}$$

Curves (b) in Fig. 1(A–C) display $\langle\sigma_b(h)\rangle$ calculated for $T = 345$, 370 and 390 K, respectively.

The solutions are given by the intersects of $\langle\sigma_a(h)\rangle$ and $\langle\sigma_b(h)\rangle$. For $T = 345$ and 390 K there is only one solution whereas for $T = 370$ K there are three solutions.

In Fig. 2 we compare the results provided by this technique and by the exact 1D treatment (transfer matrix technique). We have used the thermodynamic parameters of the $[Fe(Htrz)_2(trz)](BF_4)_2$ compound [2,4]. An excellent agreement is obtained.

In Fig. 3 we show the results obtained for 2D systems (here a square lattice 8 × 8 with periodic conditions). In this case we have fixed the long-range interaction ($G =$ 105 K) and we have taken six different values for the short-range interaction J ($J = 10$, 20, 40, 100 K). Δ and g_{HS}/g_{LS} have been taken for a type 2D spin crossover system: $[Fe(btr)_2(NCS)_2]\cdot H_2O$ [18]. According to the values of J a S-shape or a Z-shape is obtained. This result generalises the previous conclusion, obtained for 1D systems, that the squareness of the thermal hysteresis loop should be related to the presence of short-range interactions. A similar conclusion is expected for 3D systems, and will be reported as soon as obtained.

5. Conclusion

Monte Carlo entropic sampling together with 'a self-consistent technique' proves to be a useful way to simulate thermal behaviour of the fictitious magnetisation of spin crossover molecules (1D- and 2D-systems). An excellent agreement is obtained with transfer matrix technique for 1D system.

In 2D spin crossover systems, for a given value of the long-range interaction G, the hysteresis curve changes from S-shape to Z-shape when increasing short-range interaction J. This result generalises the conclusion obtained previously for a 1D system [2].

This technique can also be applied for other Ising systems (honeycomb, cubic lattice,...) as well as for a Blume-Capel model (for a three-state system).

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