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Abstract. This contribution deals with the development of a 3D Monte Carlo (MC) entropic sampling algorithm to evaluate the density of states of a SCO nanoparticles using three parameters related to the "magnetization", the "spin-spin correlation" and the number of molecules at the surface. This information is then used to analyze the role of the interaction parameter, L, between the external environment of the nanoparticle and the surface's molecules. We show that increasing "L" shifts downward the system's transition temperature, generating a thermal hysteresis whose width increases linearly with the strength of this parameter "L". These behaviors are also studied as function of the SCO nanoparticle size.

Keywords: Monte Carlo simulations, entropic-sampling algorithm, spin-crossover, phase transition, thermal hysteresis

1. Introduction

Spin crossover (SCO) compounds [1-6] exhibit a thermal transition between two states: High-spin (HS) and Low-spin (LS) states. The LS to HS transition temperature, T_{up}, on heating mode is higher than the HS to LS transition temperature, T_{down}, on cooling mode. The width $\Delta T=T_{up} - T_{down}$ characterizes the thermal hysteresis and is usually related to strength of the interactions in the system. To simulate thermal or pressure behavior of nanoparticles using all the spin configurations, an entropic sampling technique has been developed and applied to 2D SCO nanoparticles configuration. In this contribution we have extended our previous entropic sampling method [7,8] to the 3D cases.

2. Monte Carlo entropic sampling method

The thermal hysteresis in the SCO compounds are the fingerprint that the system goes through metastable states along its thermal transition between the low-spin and the high-spin states. To study the size and shape effects on the width of the hysteresis, we have developed an entropic sampling technique that provides access to the density of states of all the macro-states contrary to the Metropolis technique which mainly selects the configurations with high Boltzmann factor.

In the framework of the Ising-like model [9-12] the two spin states of the spin-crossover molecule, namely the High-Spin (HS) and the Low-Spin (LS) states, are represented by a fictitious two-states operator σ with respective eigenvalues: - 1 (LS) and +1 (HS) with associated degeneracies g_{LS} and g_{HS} respectively.

The Hamiltonian operator, which includes the short (J) and long (G) –rate interactions as well as the matrix effect represented by the interaction parameter, L, writes as:

$$H = \frac{\Delta - k_B T \ln g}{2} \sum_{i=1}^{N} \sigma_i - G \sum_{i=1}^{N} \sigma_i < \sigma > - J \sum_{<i,j>} \sigma_i \sigma_j - L \sum_{k=1}^{M} \sigma_k \quad (1)$$

Where, the energy gap Δ (> 0) between LS and HS states is such that the LS state is the ground state at 0K; $< \sigma >$ is the thermal average value of the operator σ , g = g_{HS}/ g_{LS} is the ratio between the degeneracies of the HS and LS states; N is the total number of the molecules and M is the number of molecules at the surface, whose their spin states are represented by the specific operator, σ_c.

Using the following parameters, $m = \sum_1^N \sigma_i$, $s = \sum_{\langle i,j \rangle} \sigma_i \, \sigma_j$, $c = \sum_1^M \sigma_c$, the total Hamiltonian (1) can be written as:

$$H = -h\, m - J\, s - L\, c \quad (2)$$

where $h = -\frac{\Delta - k_B T \ln(g) - 2\, G \langle \sigma \rangle}{2\, k_B T}$ is the effective ligand field.

The thermal average value of σ, which is the average net fictitious magnetization, is calculated through the expression:

$$\langle \sigma \rangle = \frac{\sum_1^{NL} \frac{m}{N} \mathrm{d(m,s,c)} \exp(-\beta\, (-h\, m - J\, s - L\, c))}{\sum_1^{NL} \exp(-\beta\, (-h\, m - J\, s - L\, c))} \quad (3)$$

where NL is the total number of the different configurations of the triplet (m, s, c), β = 1 / k_BT and d(m,s,c) is the density of states of each macro-state (m,c,s). The purpose of the entropic sampling method is to calculate d(m,s,c). At this end, the Monte Carlo procedure is biased by introducing the following distribution:

$$P_{m,s,c} = \frac{1}{d(m,s,c)} \quad (4)$$

in the detailed balance equation

$$P_{m,s,c}\, W_{(m,s,c) \to (m',s',c')} = P_{m',s',c'}\, W_{(m',s',c') \to (m,s,c)} \quad (5)$$

We perform only once the Monte Carlo to fill up the d(m, c, s) table, from which, the average magnetization <σ>, the partition function Z as well as the others thermodynamic properties of the systems can be calculated for any temperature, interactions, energy gap, degeneracies values.

3.Results and discussion

Figure 1 summarizes the size effects on the thermal spin transition without any matrix effect (L=0). Thus, a SCO nanoparticle with 4x4x6 size, displays a thermal hysteresis in the thermal evolution of the average high spin fraction Nhs defined as $Nhs = \frac{1+<\sigma>}{2}$. The width of this hysteresis reduces for a smaller nanoparticle (4x4x5 size) and even disappears for the particles of size 4x4x4 and 4x4x3. This result is quite natural, and supports the idea that the existence of metastable states (and so the thermal hysteresis) in this model strongly depend on the system size which needs a threshold free energy barrier to stabilize them against the MC fluctuations. Although the bulk sites play in favor of the first order transition, surface atoms whose ratio increases with decreasing the size favor the gradual transition behavior due to the lack of neighboring sites. Because, the absence of the environment effects, the equilibrium temperature remains the same, and does not depend on size, as is shown in Fig 2 and in table 1.

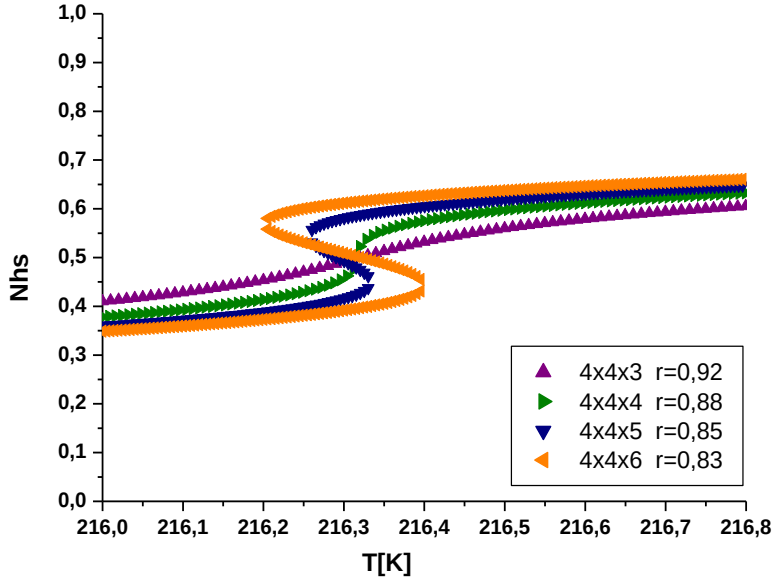

Figure 1. Thermal evolution of the high spin fraction for different sizes of the 3D SCO nanoparticle configuration: 4x4x3 (purple up triangle), 4x4x4 (green right triangle), 4x4x5 (blue down triangle), 4x4x6 (orange left triangle). The computational parameters are: Δ/k_B = 1300 K, J/k_B = 20 K, G/k_B = 133 K, L/k_B = 0 and ln(g) = 6.01. The ratio between surface and volume numbers of the molecules is denoted by r.

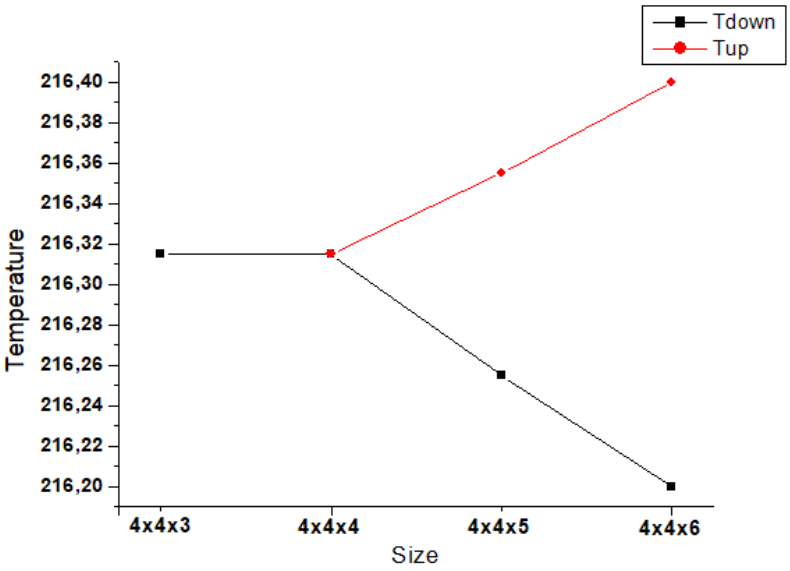

Figure 2. Size dependence of the lower (T_{down}) and upper (T_{up}) transition temperatures of the thermal HS fraction of Fig. 1. A clear linear change of the thermal hysteresis width as function of size is revealed.

Table 1 . T_{down} , T_{up} and $T_{equilibrium}$ for different SCO 3D nanoparticles corresponding to Figs. 1 and 2.

SIZE	Tdown	Tequilibrium	Tup
4x4x3		216.315	
4x4x4		216.315	
4x4x5	216.255		216.355
4x4x6	216.2		216.4

To study the role of the matrix effect, we fix the size of the SCO nanoparticle configuration to 4x4x5 and we decreased the value of the long-range interaction from 133 to 125 K, compared to the studied case of Fig. 1. As a result, in the absence of this environmental interaction (L=0) the system does not display the thermal hysteresis. When we increase the L value, the effective ligand of surface atoms decreases, which favors the appearance of the first-order transition and the enhancement of the thermal hysteresis width, due to the long-range interactions (G parameter). Fig 3 and Fig 4 display the thermal evolution of the HS fraction as well as the width of the thermal hysteresis for different values of L parameter.

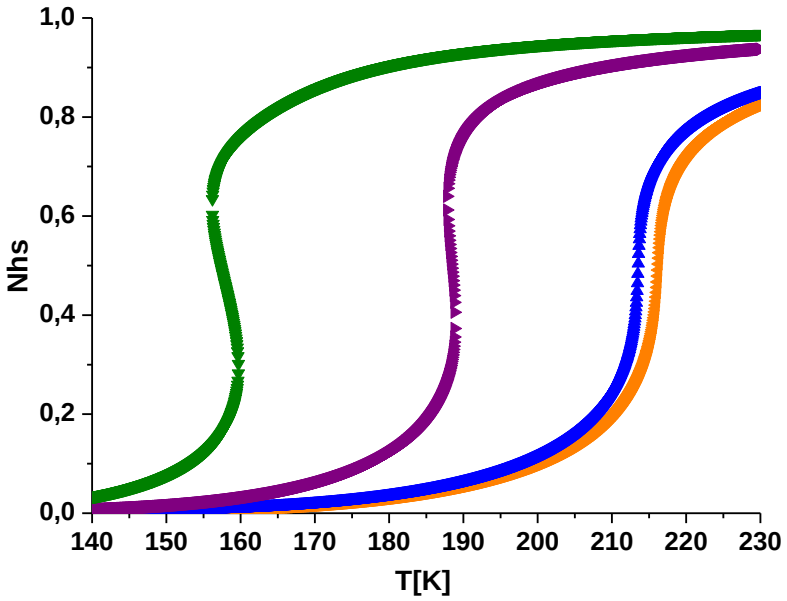

Figure 3. Thermal evolution of the HS molar fraction Nhs in a 4x4x5 3D SCO nanoparticle configuration for different values of the interaction with the surroundings: L/k_B =0 (orange triangle), L/k_B =10 (blue up triangle), L/k_B =100 (right purple triangle), L/k_B =200 (green down triangle). The computational parameters are: Δ/k_B = 1300 K, J/k_B = 20 K, G/k_B = 125 K and ln(g) = 6.01. The ratio r between surface and volume numbers of molecules is: r = 68 /80 = 0.85

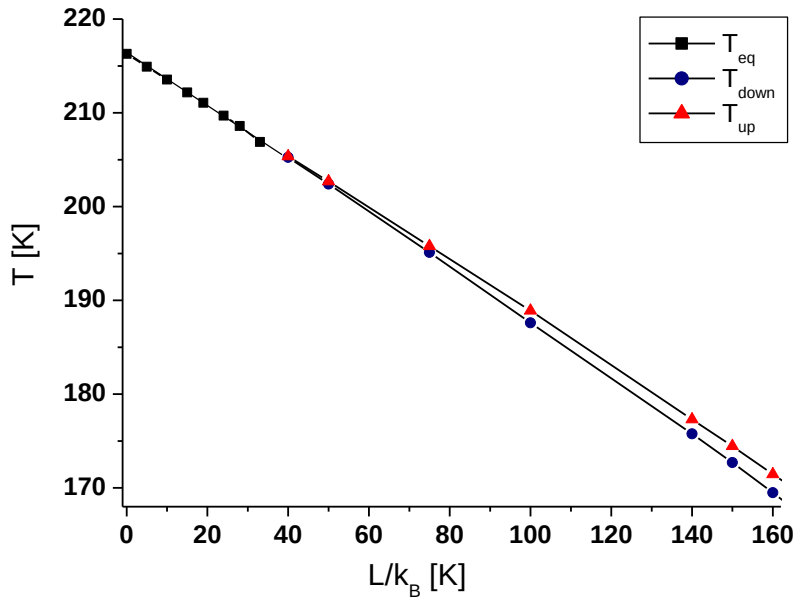

Figure 4. Evolution of the width of the thermal hysteresis as a function of L/k_B parameter. The computational parameters are : Δ/k_B = 1300 K, J/k_B = 20 K, G/k_B = 133 K, and ln(g) = 6.01

4.CONCLUSION

The entropic sampling with three macroscopic parameters, m, s and c, corresponding respectively to average values of the total magnetization, short-range correlations and surface magnetization, allows the study of 3D SCO nanoparticles configurations with short- and long-range interactions as well as an interaction with the immediate environment of the nanoparticles. This last effect, denoted here matrix effect, is at the origin of the re-emergence of a new thermal hysteresis whose existence is due to the interaction between the molecules at the surface with their environment.

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