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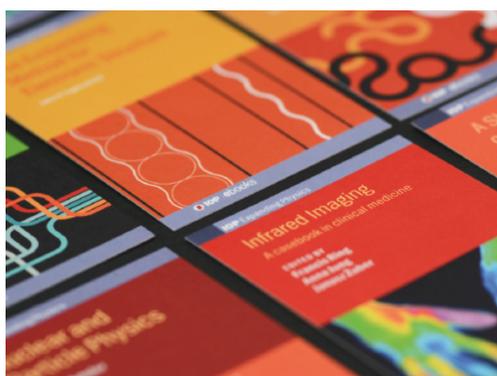
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Analysis of hysteretic spin transition and size effect in 3D spin crossover compounds investigated by Monte Carlo Entropic sampling technique in the framework of the Ising-type model

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Abstract. In spin crossover (SCO) systems, the shape of the hysteresis curves are closely related to the interactions between the molecules, which these play an important role in the response of the system to an external parameter. The effects of short-range interactions on the different shape of the spin transition phenomena were investigated. In this contribution we solve the corresponding Hamiltonian for a three-dimensional SCO system taking into account short-range and long-range interaction using a biased Monte Carlo entropic sampling technique and a semi-analytical method. We discuss the competition between the two interactions which governs the low spin (LS) - high spin (HS) process for a three-dimensional network and the cooperative effects. We demonstrate a strong correlation between the shape of the transition and the strength of short-range interaction between molecules and we identified the role of the size for SCO systems.

1. Introduction

The predictions which consider that, the density of the future recording materials is approaching its limit, imply that more theoretical studies to be done to overcome this obstacle. In this respect, a close correlation between theoretical and experimental work must be established. A better understanding of the theoretical aspects, of the parameters in the network structure will lead synthetic chemistry towards elaborations of new spin crossover (SCO) materials with these different properties. In recent years the SCO phenomenon [1,2,3,4] has attracted a growing and important interest for physicists, biochemists, and chemists, since it offers an understanding of ligand field theory and the functions of molecular systems. The benefits for industrial applications are benefiting for data storage, fast sensors, memory devices or biological imaging.



The (Fe^n) SCO compounds contain bistable molecules which can exist in two different states: a diamagnetic low-spin state (LS) and a paramagnetic high-spin state (HS). Depending on certain factors (like temperature, pressure, magnetic field, ultra-short laser pulse, X-ray radiations, electrical field [5]) the states can switch. As a response to these factors, the LS-HS or HS-LS transition involves both structural changes and electronic transformations. Regarding the shapes of the spin transition, the Fe^n SCO compounds can present a gradual, abrupt, with hysteresis, or into two-step shape. The last two shapes, which results when the system confers a bistability as a function of some external factors (usually temperature), represent one of the most pregnant aspect of spin crossover phenomenon.

Nowadays SCO compounds have been studied intensively, and many studies and topics have present the influence of some external stimuli as temperature, magnetic field, pressure, light on the SCO behavior. Understanding and controlling the properties of bistable complexes, also involve studying the influence of the cooperative interaction between the molecules. It is well known [1] that hysteresis in a spin transition curve has two causes. The first one came from the phase change in the lattice and the second one come from the elastic interaction between neighbouring molecules in the network. Taking into account the second hypothesis, in this paper we study a spin transition accompanied by a hysteresis loop and we show the importance of the strength of short-range interaction in understanding the properties and predicting the behavior of SCO compounds [6, 7].

In our study we use the variation in temperature (one of the most common perturbation factor which influences the change spin state process) and an Ising-like model. On the basis of good agreement between simulated results and experimental ones, we considerate in the Ising Hamiltonian both short range and long range interactions as well as distinct degeneracies between the molecular states [6].

The article is organized as follows: in section 2, we present and explain the Ising-like model with both short range (J) and long range (G) interactions. In section 3 we present how the partition function formula with the contribution of Monte Carlo (MC) entropic sampling method is realized. We also present the role of the short-range interactions and an analysis of the system behavior as a function of several physical parameters. In section 4 we present how the number of molecules influences the cooperative phenomena. The last section ends with conclusions.

2. The model

In recent years a variety of models (Bragg-Williams models [8], Ising models [9, 10], atom-phonon (APC) model [11, 12, 13, 14, 15, 16, 17, 18, 19] or mechano-elastic model [20, 21]) and studies have been performed to explain the LS-HS transitions, which appear in some molecular solids. It is well known that these switching processes appear in the SCO compounds which contain metal ions with $d^4 - d^7$ electron configuration in an octahedral symmetry environment. According to how the electrons occupy and move between the e_g and t_{2g} orbitals, the two LS and HS states, for Fe^n , can be defined as follows:

- The Fe^n is in the LS state when all the six electrons occupy the three orbitals of the lowest energy. In this case, the spin paring energy (Δ) is less than the ligand field splitting energy (δ).
- The Fe^n is in the HS state when five electrons occupy all the five orbitals and sixth electron will be in of the lowest energy orbital. In this case the ligand field splitting energy(δ) is less than spin paring energy (Δ)[figure 1]

The thermodynamic competition of these two states (LS and HS) can be characterized by the proportion of molecules in the HS state, denoted here as n_{HS} .

We would like now to explore further this n_{HS} distribution as a function of the temperature. To do this, we will adopt a two level model (Ising model) in which we consider a three dimensional network with free boundary conditions. Figure 2 shows a random configuration for $3 \times 3 \times 3$ (27 molecules) system.

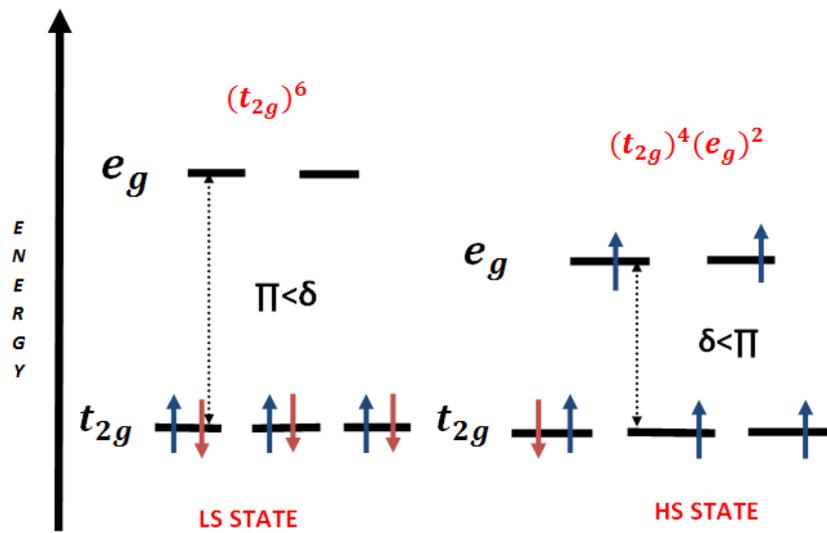


Figure 1. Distribution of electrons over 3d orbitals in low-spin state and high-spin state, for Fe^{2+} .

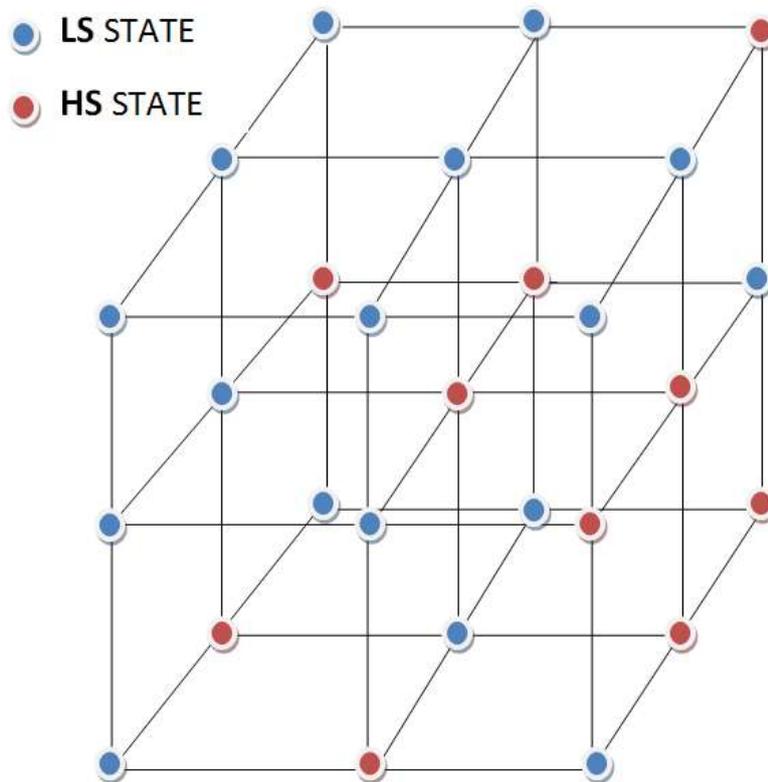


Figure 2. A three-dimensional (3x3x3) network containing twenty-seven molecules chosen arbitrarily.

Taking into account that: (1) to each molecule we can associate a fictitious spin operator " σ " with two eigenvalues (-1 for LS state and +1 for HS state);(2) Δ is the energy gap between the HS state and LS state; (3) $g_{state} = \left(\frac{g_{HS}}{g_{LS}} \right)$ (g_{HS} is the degeneracy of the HS state and g_{LS} is the degeneracy of the LS state); and (4) J is the short-range interactions and G represent the long-range interactions the Ising Hamiltonian can be written as[6]:

$$H = -h_f \sum_{i=1}^N \sigma_i - J \sum_{\langle i,j \rangle} \sigma_i \sigma_j \quad (1a)$$

where:

$$h_f = - \left(\frac{\Delta - k_B T \ln(g_{state})}{2} - G \langle \sigma \rangle \right) \quad (1b)$$

$-k_B$ is Boltzmann's constant and T is the temperature of the system.

3. Analysis of the method and short-range interaction effect

In this work we adopt a consistent method based on the bisection method [22] and we show the evolution of n_{HS} , high-spin fraction, as a function of temperature for different physical parameters values.

Using equation 1b and taking into account that $n_{HS} = (1+\sigma)/2$, we can define the high-spin fraction corresponding to the Ising Hamiltonian as:

$$n_{HS}^1 = \frac{1 + \frac{h_f}{G} + \frac{\Delta - k_B T \ln(g_{state})}{2G}}{2} \quad (2)$$

If we consider a system of equations, we will need now a second function n_{HS}^2 to find the solutions.

The n_{HS}^2 fraction can be found from the MC entropic sampling method [23, 24]. This method has been used by Linares et al.[22] who showed that, by comparison to exact solution for a one dimensional network (1D systems), that this MC entropic sampling method gives the same results. In this article we apply this technique to a three dimensional network and we show that the hysteresis loop width is correlated to the short-range interaction strength.

Taking into account that $d(m,s)$ is actually the degeneracy of the macrostate (m, s) where m and s are two macroscopic variables $m = \sum_{j=1,N} \sigma_j$; $s = \sum_{\langle i,j \rangle} \sigma_i \sigma_j$ the expression for n_{HS}^2 is :

$$n_{HS}^2 = \frac{\sum_{j=1,N} \frac{m_j}{N} d(m_j, s_j) \exp(-\beta(-h_f m_j - J s_j))}{\sum_{j=1,N} d(m_j, s_j) \exp(-\beta(-h_f m_j - J s_j))} \quad (3)$$

where $\beta=1/k_B T$;

Taking into account the expressions of n_{HS}^1 and n_{HS}^2 we can construct the graph for each temperature.

Figure 3 displays the n_{HS} as a function of effective field h_f (equation 1b). The graphic for temperature $T=110K$ is represented in Figure (3a). In this case because the two curves (n_{HS}^1 and n_{HS}^2) intersect at only one point, this will be the solution. In this case the intersection point (point A) is a stable point and can also be indentified in figure 4.

Now for other temperatures we can also have one solution (point E) for $T=240\text{K}$ or three-solutions (points B, C, D) for $T=160\text{K}$. For $T=240\text{K}$ (figure 3b) it can be observed that we have also a stable point (point E) but with another n_{HS} associates [for point A the n_{HS} is equal to 0. and for point E the corresponding n_{HS} is equal to 0.99]. When three solutions are obtained, as for $T=160\text{K}$ (figure 3c) we will have:

- point B – stable solution with $n_{HS} = 0$.
- point C – unstable solution with $n_{HS} = 0.72$
- point D – metastable solution with $n_{HS} = 0.99$

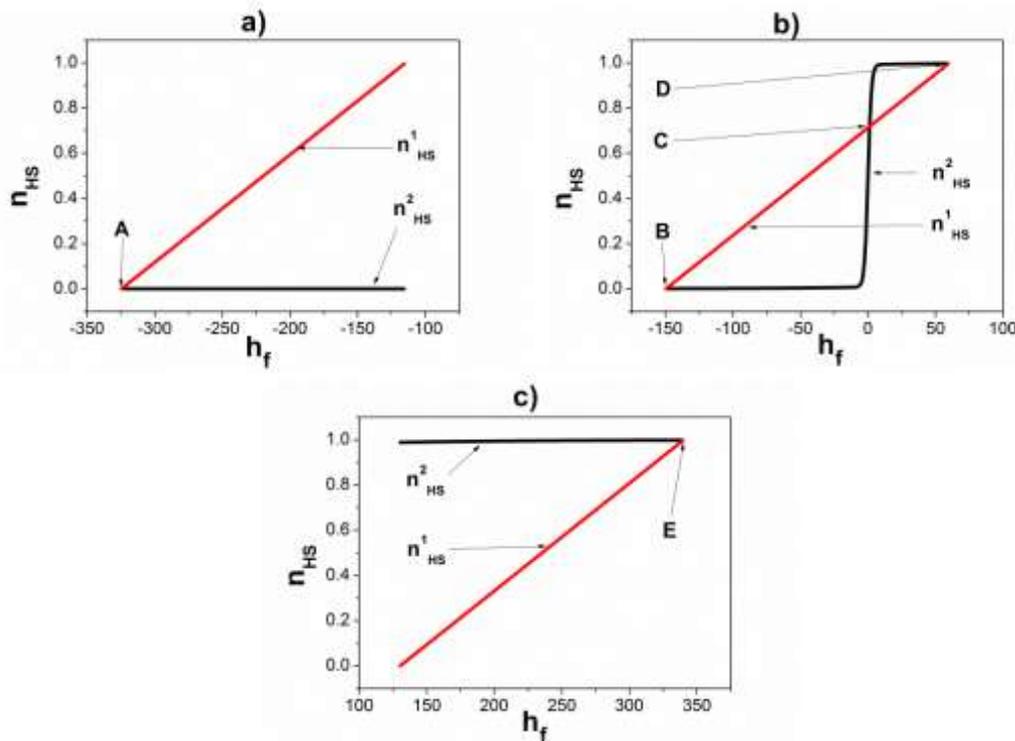


Figure 3. Evolution of HS fraction n_{HS} for a 3D system (64 molecules) with open boundary conditions for $T=110\text{K}$ (a) $T=160\text{K}$ (b) $T=240\text{K}$ (c). The parameter values are $\Delta=1209\text{K}$, $\ln(g_{state})=7$, long-range interaction is $G=105\text{K}$ and the short-range interaction is $J=100\text{K}$.

Figures 4, 5, 6, 8 displays the evolution of HS fraction n_{HS} as a function of temperature and are made in the manner already described.

To study the behavior of SCO complex, it is considered that: T_{up} is the ascending thermal transition temperature, T_{down} is the descending thermal transition temperature and $T_{1/2}$ is the average temperature between T_{up} and T_{down} . For a short-range interaction (J) equal to 100K and a long-range interaction (G) equal to 105K , then figure 4 is obtained. In this figure if we consider that ΔT is the hysteresis width and represent the difference between the ascending thermal transition temperature (T_{up}) and the descending thermal transition temperature (T_{down}), then a hysteresis of $\Delta T=53\text{K}$ is observed which

corresponds to $T_{up}=198\text{K}$ and $T_{down}=145\text{K}$. Moreover in this case when the system is formed by 64 molecules it can be observed that $T_{1/2}$ is equal to 171.5K.

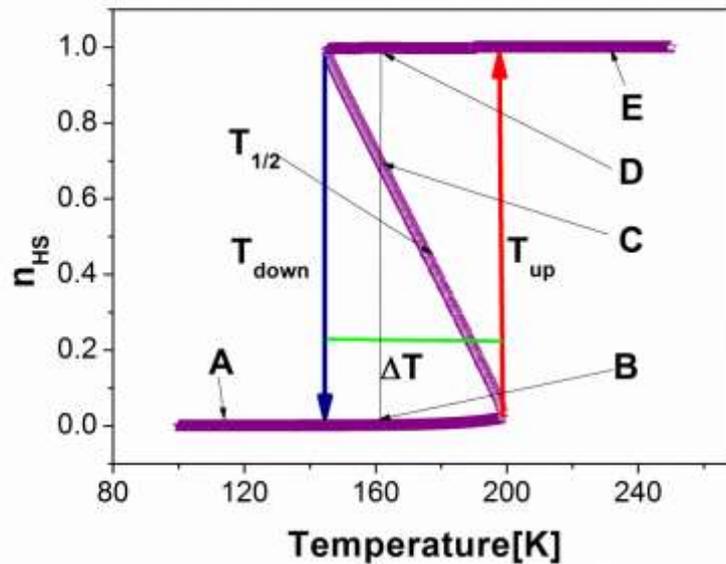


Figure 4. Evolution of HS fraction n_{HS} as function of temperature, for a 3D system (64 molecules) with open boundary conditions. The parameter values are $\Delta=1209\text{K}$, $\ln(g_{state})=7$, long-range interaction is $G=105\text{K}$ and the short-range interaction is $J=100\text{K}$.

When the short-range interactions are decreased to $J=30\text{K}$ (figure 5) we report also a decrease in the hysteresis loop dimension from $\Delta T=53\text{K}$ to $\Delta T=8\text{K}$. In this case even if the temperature $T_{1/2}$ remains the same as in the previous example (figure 4) the ascending temperature T_{up} and the descending temperature T_{down} are changing. Now T_{up} is equal to 175K, T_{down} is equal 167K and the hysteresis width $\Delta T = 8\text{K}$.

When the short-range interaction is decreasing further, to $J=10\text{K}$ (figure 6), the interactions are not strong enough to produce a hysteretic behavior and the transition shape now have a new shape compared to that of figure 4.

It can be seen in figure 4, when the system presents a strong short-range interaction equal to 100K the shape of the transition is a “Z” shape and when the interaction between the molecules is decreasing $J=30\text{K}$ then the transition resembles a called “S shape” in some article (see figure 5).

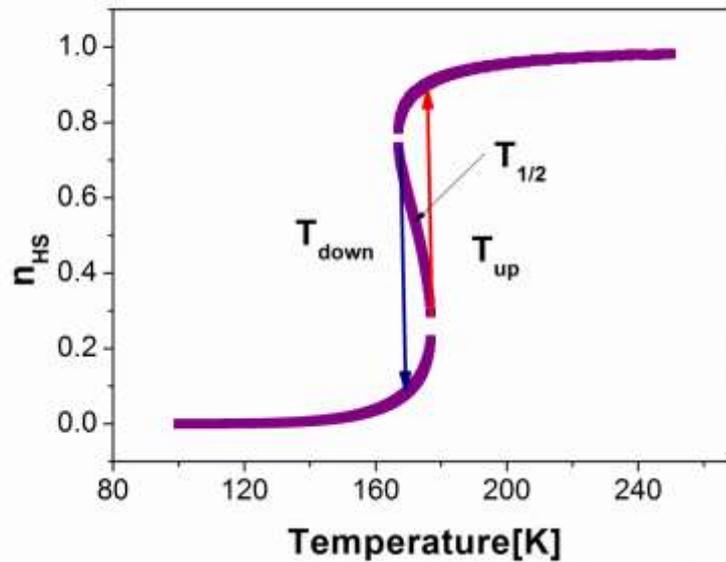


Figure 5. Evolution of HS fraction n_{HS} as function of temperature, for a 3D system (64 molecules) with open boundary conditions. The parameter values are $\Delta=1209\text{K}$, $\ln(g_{state})=7$, long-range interaction is $G=105\text{K}$ and the short-range interaction is $J=30\text{K}$.

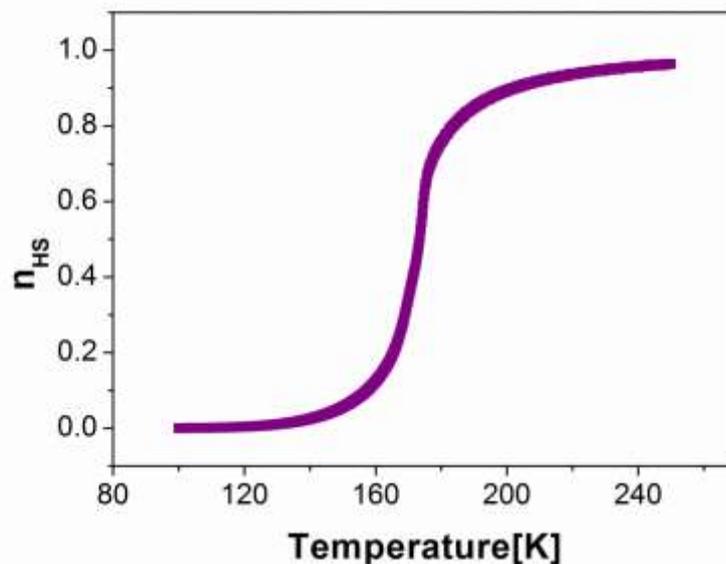


Figure 6. Evolution of HS fraction n_{HS} as function of temperature, for a 3D system (64 molecules) with open boundary conditions. The parameter values are $\Delta=1209\text{K}$, $\ln(g_{state})=7$, long-range interaction is $G=105\text{K}$ and the short-range interaction is $J=10\text{K}$.

The hysteresis loop width for different short-range interactions is presented in figure 7. In this case, the system will have a hysteresis width ΔT equal to 53 K corresponding to $T_{up} = 198\text{ K}$ and $T_{down} = 145$

K, for long-range interactions $G = 105\text{K}$ [X point]. When these interactions decrease to 10K ($J = 10\text{K}$), the hysteresis loop width ΔT will be equal to 0K [Y point].

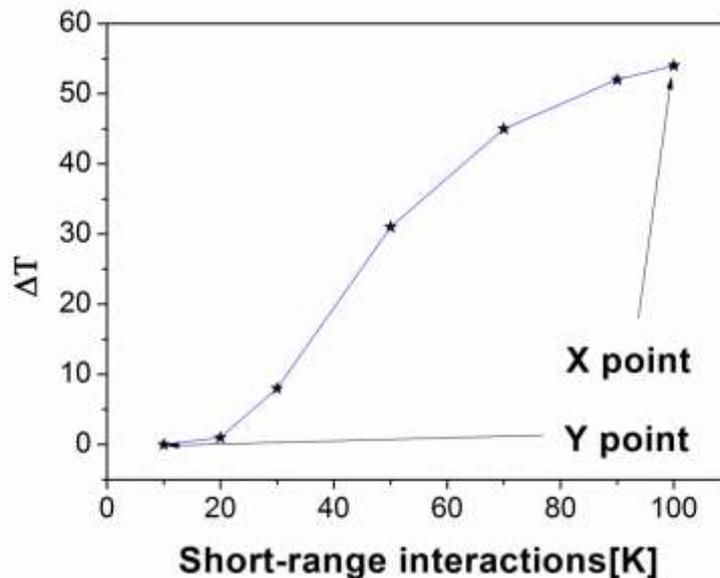


Figure 7. Evolution of hysteresis loop width ΔT vs. short-range interaction parameter J . The parameter values are $\Delta = 1209\text{K}$, $\ln(g_{state}) = 7$, long-range interaction is $G = 105\text{K}$.

4. Size effect

A similar behavior [figure 8] has been noticed, when the intensity of the short-range interactions is changing for a one or two dimensional network [22]. In this contribution we also fix the interactions and we change only the number of molecules N . Here, when the number of molecules of the system is increasing, the interactions will be stronger and a S shape will appear. For another set of parameters, for example, if is increased the short-range interactions [$J_1 = x * J$ (with x take values from 0 to ∞ , $J = 1\text{K}$)], this “S shape” will transform to a “Z-shape” as in figure 4.

Figure 9 presents the evolution of the hysteresis loop width for different sizes and short-range interactions. The hysteresis width increases, with the number of molecules, and as a function of the strength of short-range interactions for $N = 216$ molecules we have different values. When between the molecules is considerate a short-range interactions $J = 17\text{K}$ we can observe for $N = 8$ and $N = 27$ molecules, that, the system don't present hysteresis. For the same short-range interactions system present a hysteresis loop equal to 1K when the number of the molecules is $N = 216$ molecules.

Moreover when the short-range interactions is increased to $J = 22\text{K}$ for $N = 8$ molecules there will be no hysteresis but for $N = 27$ molecules there will be a hysteresis loop equal with 1K . In this case it can be observed, the fact that, a system with $N = 27$ molecules and a short-range interaction between molecules of $J = 22\text{K}$, have the same hysteresis loop dimension as a system with $N = 216$ molecules but with a less short-range interaction ($J = 17\text{K}$).

Concerning the number of molecules (size effect) for a system, other studies have been performed by Rotaru et al. [19,26] using the FORC technique and by Murukoa et al.[27] taking into account the edge effect. In all cases it was shown that number of molecules (system size) influence the hysteresis loop dimension.

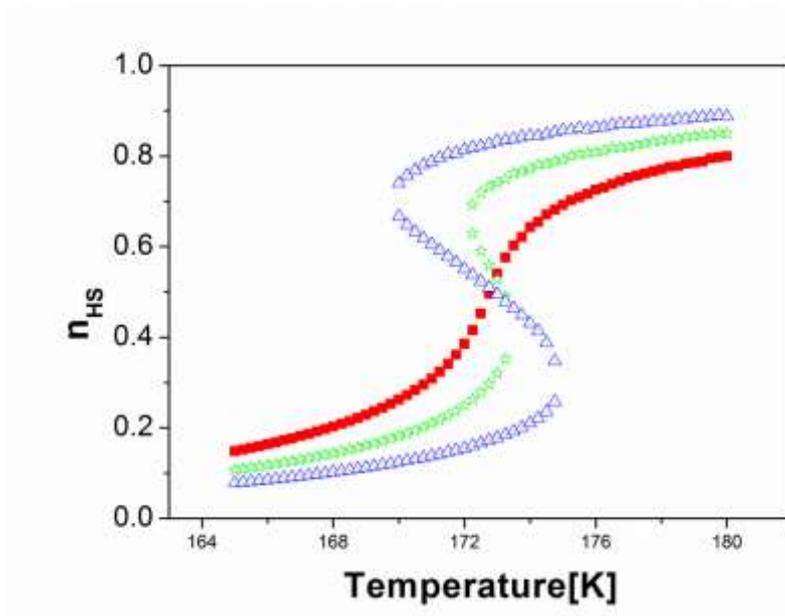


Figure 8. Evolution of HS fraction n_{HS} as function of temperature, for a 3D system with different number of molecules $N=216$ (triangle), $N=64$ (stars) $N=8$ (square) with open boundary conditions. The parameter values are $\Delta= 1209\text{K}$, $\ln(g_{state})= 7$, long-range interaction is $G=105\text{K}$ and the short-range interaction is $J= 22\text{K}$.

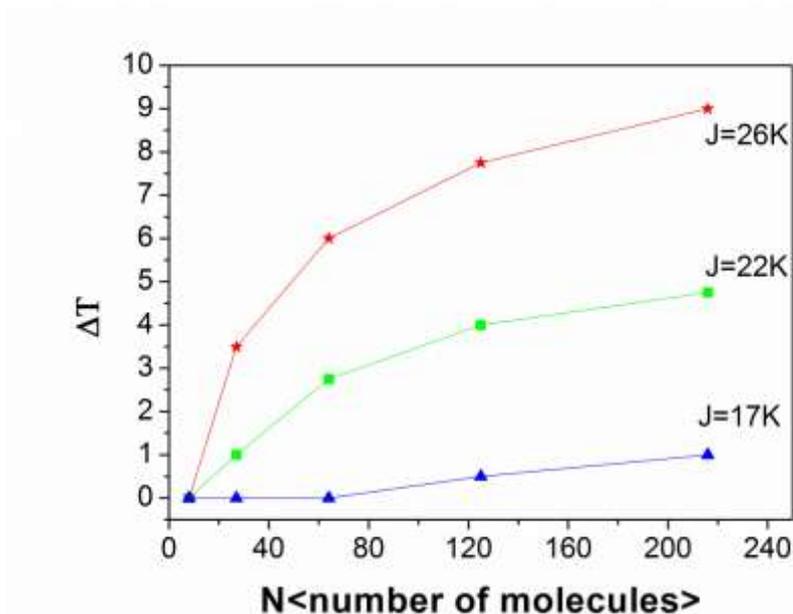


Figure 9. Evolution of hysteresis loop width ΔT vs. number of molecules for different short-range interaction strength. $J=17\text{K}$ (triangle), $J=22\text{K}$ (square) $J=26$ (stars). The parameter values are $\Delta= 1209\text{K}$, $\ln(g_{state})= 7$, long range interaction is $G=105\text{K}$.

5. Conclusions

We have used Ising-type model with short-range and long-range interactions to investigate the influence of the short-range interactions and of the system size on a three-dimensional system. Applying MC entropic sampling technique to a 3D SCO complex proves to be a good way to characterize the hysteretic spin transition behavior.

Another result obtained is the changing of hysteresis curves from a Z shape to a sinusoidal(S) shape when the short-range interactions are decreasing. This behavior has been also obtained by Linares et al.[6] for one-dimensional $[Fe(Htrz)_2(trz)(BFA)_2]$ compound or two-dimensional $[Fe(btr)_2(NCS)_2H_2O]$ compound. And finally we have found and confirm the hypothesis [25, 26] that, *the hysteresis width decrease as of number of molecules is reduced.*

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