

ELASTIC MODEL FOR SPIN CROSSOVER NANOPARTICLES IN MATRICES

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Abstract. In this paper we investigate the thermal behaviour of spin crossover nanoparticles in matrices formed by polymer or surfactant molecules using an elastic model. The individual molecules are represented as balls with different sizes depending on the spin state and the intermolecular interactions are taken into account by the way of springs with given elastic constant. The surrounding matrices are represented as lattices of given size molecules, linked by springs. The system is treated in the framework of Monte Carlo Method with Arrhenius probabilities. The main objective is represented by the understanding of the differences in behaviour between nanoparticles compared to bulk of the same material. In addition, we study the effects of the size of matrix molecules and we discuss the mechanism of propagation of spin change from a particle to another through the matrix.

Key words: spin crossover nanoparticles, elastic model, Monte Carlo simulation, cluster formation.

1. INTRODUCTION

Spin crossover molecular magnets are molecular inorganic compounds of transition metals having 4 to 7 electrons on their last d level, situated in an octahedral environment. They show a thermal switch between the paramagnetic high-spin (HS) state, stable at higher temperatures and the diamagnetic low-spin (LS), stable at lower temperatures. If the intermolecular interactions of steric origin between spin crossover units are strong enough, a first order phase transition with the temperature (or light irradiation, or pressure) is observed. It is often accompanied by steep and large hysteresis loops favouring the possibility of a multitude of applications, which include, but are not limited to, full optical memories or sensors.

Similar to recent general tendencies in material sciences, the miniaturization of spin crossover compounds has become increasingly important in the last few years. The study of spin crossover nanoparticles, obtained by various groups [1–4] revealed several somewhat unexpected differences compared to the bulk compounds, like the shift of the thermal transition towards lower temperatures, smaller hysteresis loops (if any) with more gradual and sometimes incomplete transitions, and large residual HS fraction at lower temperatures. At the same time, a similar behaviour has been observed for the bistability properties of an iron(II) spin-transition microparticles, embedded in suitable environment (polymer or other dispersant, denoted here as matrices) (Fig. 1a) [5]. Among the large number of models used to describe the behaviour of spin crossover compounds, only a few proved to be efficient in describing the peculiarities of spin crossover nanoparticles. Following an initial Ising-like model, based on a three-dimensional open boundary structure with short-range interactions, which succeeded to reproduce only the decreasing of the hysteresis width [6], static Ising-like models [7] taking into account specific interactions between border spin crossover molecules and polymer molecules [8] or forced HS state molecules [9] have successfully accounted most of experimental features. Recently, more realistic approaches to this problem have been realized using elastic models [10] by taking into account the flexibility of the spin crossover structures. Up to now, the models have been focussed on the study of isolated spin crossover nanoparticles situated in glass forming, polymer or surfactant matrices – the few studies using Ising or elastic models of ensembles of non-interacting particles can be regarded as a multiplication of the study of single particles.

Here we discuss the case of spin crossover particles dispersed in matrices – which can be glasses, polymer or surfactant – taking into account the propagation of interactions from particle to particle through

matrix as elastic waves. The paper is structured as follows: first we present the model and justify its convenience for spin crossover compounds, then we apply it for simulating the macroscopic behaviour of single or multiple particles in polymers and finally we describe the microscopic cluster formation in molecules and the propagation of elastic waves through matrix.

2. MODEL

The recently developed mechanoelastic (ME) model [11–13], based on the so-called ball and spring concept, is applied here in order to reproduce the experimental facts. We have to strengthen that even if most spin crossover compounds have Fe(II) as the central ion, the intermolecular interactions are different from exchange coupling interactions in ferromagnetic materials, as the iron ions are separated by inorganic ligands. Instead, the elastic interactions inside the sample arise from the lattice distortions determined by the difference of the molecular sizes between the LS and HS states – HS state has an approximately 3% larger volume, due to the presence of electrons on antiligand orbitals [14]. Elastic models are based precisely on this phenomenology. In these models, the spin-crossover molecules are represented as rigid spheres, situated in open boundary lattices and interacting by the way of connecting springs, with a given elastic constant k . We have considered here triangular configurations, which ensure an increased stability of the system and allow the use of a single elastic constant. The volume variation of a switched molecule produces an instantaneous elastic force in its neighbouring springs and consequently determines a shift in initial position, first of its closest neighbours, and subsequently of all the other molecules in the system. Therefore, the volume and the shape of the whole system change with every molecular switch. The new position of molecules is found here by solving a system of coupled differential equations, having the elastic force as the driving parameter.

The system is treated in the framework of the classical mechanoelastic procedure, using an Arrhenius dynamics with LS→HS and HS→LS transition probabilities [11], depending on the temperature, on the intrinsic features of the spin-crossover molecules and on the interactions between molecules, represented here by the way of the local pressure – algebraic sum of all elastic forces – according to:

$$P_{HS \rightarrow LS}^i = \frac{1}{\tau} \exp\left(-\frac{E_A - \kappa p_i}{k_B T}\right)$$

$$P_{LS \rightarrow HS}^i = \frac{1}{\tau} \exp\left(-\frac{D - k_B T \ln g}{k_B T}\right) \exp\left(-\frac{E_A + \kappa p_i}{k_B T}\right),$$

where i runs over all molecules in the system, T is the temperature, p_i is the local pressure acting on the i^{th} molecule, $k_B \ln g$ is the entropy variation given by the ratio of the density of states g . E_A corresponds to the activation energy for the HS→LS relaxation for a global reference state of the system for which all the complexes are in the HS state and D corresponds to the enthalpy difference between the two states in the case of non-interacting molecules, i.e. a reference state with half of the molecules in the HS and half in the LS state randomly distributed. τ is a scaling factor, chosen so that the above probabilities are well below unity at any temperature and κ is the above mentioned scaling factor between the local pressure and its effect on the activation energy of the individual molecule. According to a standard Monte-Carlo algorithm, we check every spin crossover molecule to verify if it switches by comparing the above probabilities with a subunit random number. A Monte Carlo step is completed when all spin crossover molecules have been checked once. After every Monte Carlo step, the new equilibrium position of all molecules, either spin crossover or matrix, are found once again. For every temperature, a large number of Monte Carlo steps are considered in order to be certain that the system reaches its canonical state.

Similar to Ising-like models, the elastic models applied for open boundary spin crossover systems were able to reproduce only the less steep transition and the decreasing of the width of the thermal hysteresis with the nanoparticle size, while the shift towards lower temperature values could not be obtained (see Fig. 1b). In order to account for all experimental features, a different approach was necessary. For this, the spin crossover particles were considered as embedded in matrices [12]. The use of this approach was

motivated by the standard preparation method of spin crossover nanoparticles, which implies the use of a polymer / surfactant protected synthesis in order to obtain nanoparticles of different sizes [4, 15]. The surfactant itself forms a more or less flexible matrix around the nanoparticles, preventing the agglomeration of nanoparticles to form larger ensembles. The spin crossover molecules at the surface will therefore interact with the polymer matrix via either Van Der Waals interactions or hydrogen bonding.

In previous studies [5, 12], the system was simplified and only the first shell of the embedding matrix was taken into account, as a rigid or flexible chain of non-switching molecules that interact with the molecules situated at the edge of the lattice by way of springs (Fig. 1c) with a given elastic constant denoted as k_{pol} . When HS-LS transition proceeds, the spin crossover nanoparticle shrinks, and, if the polymer is not flexible enough, an increasing negative pressure appears at the edge of the system, originating in pulling forces from the polymer network. With this premise, the hysteresis not only shifts to lower temperatures, for moderate interactions between edge molecules and polymer, but also the transition is no longer complete and a residual HS fraction is observed, if these interactions are stronger (Fig. 1d) [4, 10].

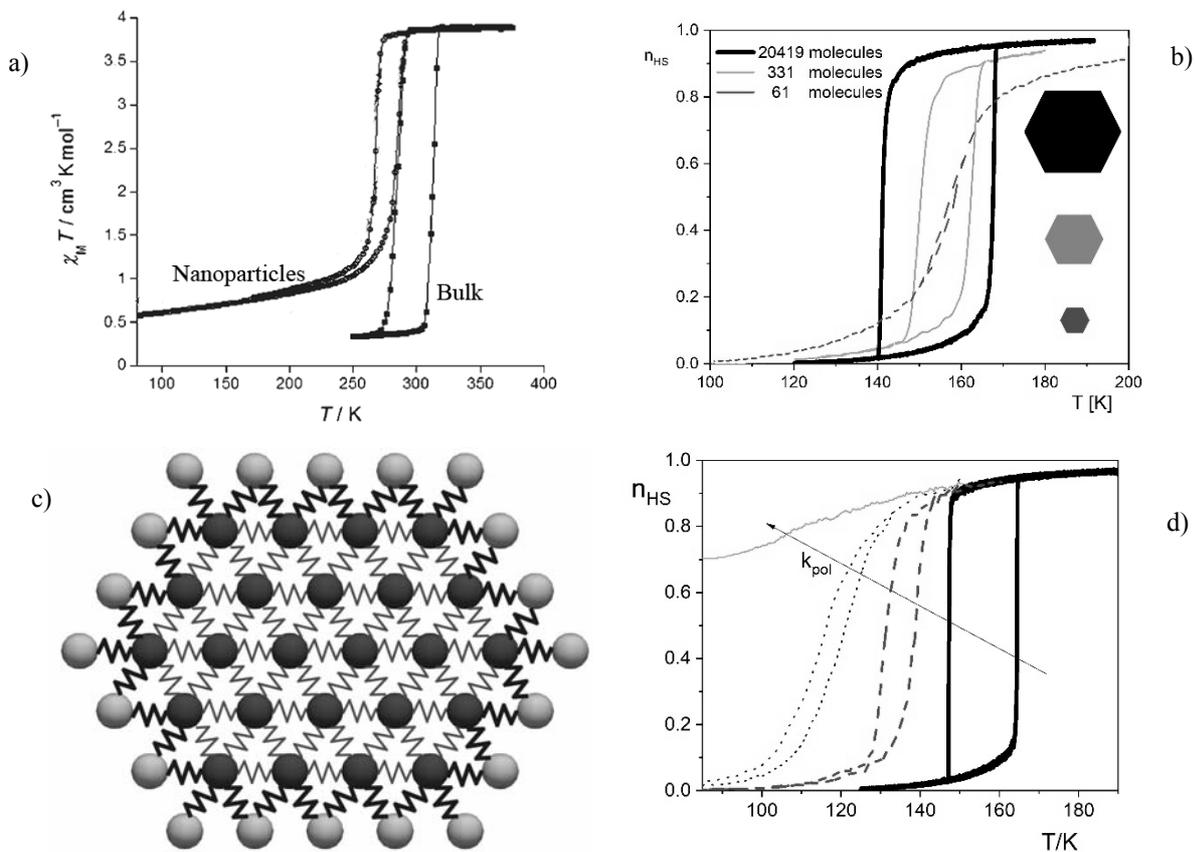


Fig. 1 – Spin crossover particles embedded in matrices: a) typical experimental data showing the differences between bulk and nanosized crystals of $[\text{Fe}(\text{pz})\text{Pt}(\text{CN})_4]$ spin crossover system (adapted from [15]); b) simulation showing the size effect for open boundary particles, in the framework of the mechanoelastic model (adapted from [12]); c) a spin crossover particle bordered by a polymer matrix single shell; d) the effect on the thermal transition for different values of k_{pol} (adapted from [5]).

This simple model has succeeded to reproduce all experimental observed differences between nanoparticles and bulk compound mentioned in the Introduction. However, the model has been less exact for the study of nanoparticles of different sizes: it was not able to reproduce neither the variation of the thermal transition temperature nor the change of the hysteresis width with the size of nanoparticles. Here the model is improved by considering not only one single shell of polymer / surfactant molecules embedding the spin crossover nanoparticle, but a full matrix of neutral embedding molecules, as shown in Fig. 2. For practical reasons, this matrix is represented as a lattice of non-switching molecules with a constant size that interact by way of springs in between and with the spin crossover molecules situated at the edge of the spin crossover particle. For the sake of simplicity, we have used the same elastic constant k_{pol} , both for matrix-matrix and

matrix-spin crossover particle interactions. Here we have considered spin crossover particles of hexagonal or circular shapes, composed each of few thousands spin crossover molecules, as specified in text.

In Fig. 3 we represent spin crossover particles with different sizes situated in similar matrix environments. The nanoparticle size influences the observed behaviour of nanoparticles in two ways. On one side, smaller sizes results in a larger percentage of edge molecules, which is the usual size effect. On the other side, the distance between the nanoparticle and the system edge varies with the nanoparticle size for the same number of total molecules. If the nanoparticle is closer to the system edge, then the system will be easier deformable when the spin crossover molecules switch from larger HS states to smaller LS states. Therefore, the size of spin crossover nanoparticles affects the way in which the matrix acts on it and furthermore influences the propagation, by phonons, of interactions between particles.

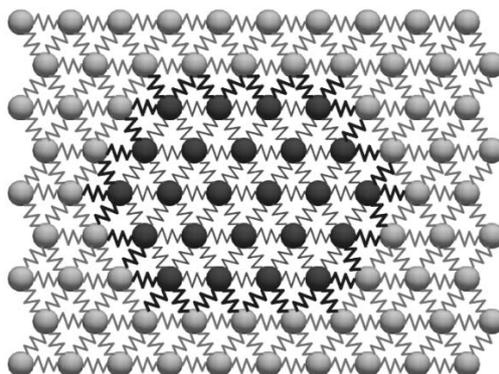


Fig. 2 – A spin crossover particle inside a polymer/ surfactant matrix.

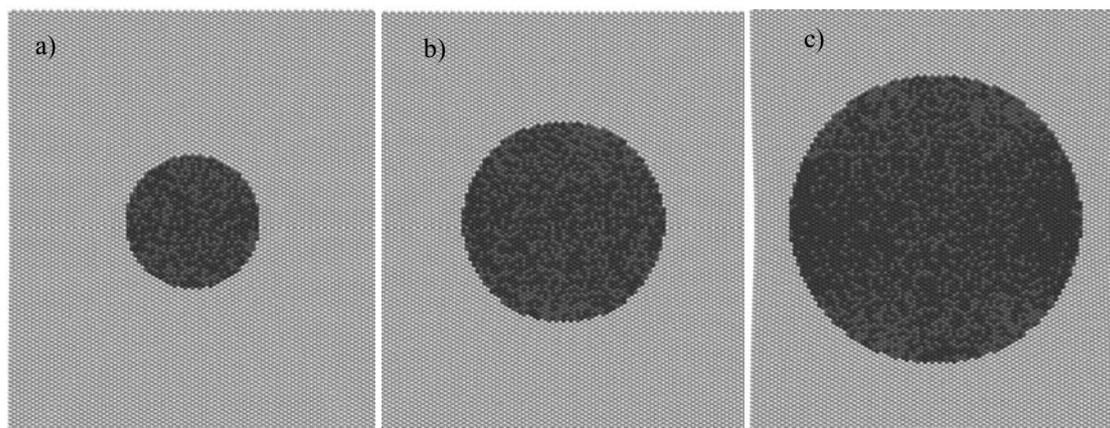


Fig. 3 – Spin crossover particles of different sizes inside a polymer matrix: a) 3945 spin crossover molecules; b) 8887 spin crossover molecules; c) 24691 spin crossover molecules. Red circles: HS molecules, blue circles: LS: molecules; grey open circles: matrix molecules. The total number of molecules (spin crossover and neutral) is 39800.

Our main goal is to establish to which extent the interaction between the spin crossover molecules and the matrix molecules influences the transition for systems composed of several spin crossover nanoparticles, separated by matrix. However, as shown in Figs. 4 and 5, it should be noted that even the simple presence of the matrix changes the transition curve and the influence of the polymer depends both on the interaction between matrix and spin crossover molecules and on the size of matrix molecules.

Therefore, we have to study first the influence of the matrix itself on the transition of a single spin crossover sample. We have considered two situations: (i) when the size of the matrix molecules is the average between HS and LS molecular sizes; (ii) when the size of the matrix molecules corresponds to the HS molecular sizes. The values of the spring constants, $k = 2N/m$, corresponds to a moderately strong elastic interaction, similar to that obtained by the estimation of the ligand field strength [13], with the bond-length difference between the HS and LS molecules $\Delta r_{HL} = 0.2 \times 10^{-10} \text{ m}$; the other parameters used in the simulation do not correspond to a specific spin crossover system but are in line with values found for several

spin crossover systems [14, 16] or used in Ising-like models $D = 1100$ K, $E_A = 400$ K, $g = 1096$, giving a thermal transition for the bulk centred around 155 K. In the first situation (Fig. 4), k_{pol} varies in the limits given by k while the transition temperature does not change, but the transition becomes smoother and the hysteresis vanishes for large k_{pol} .

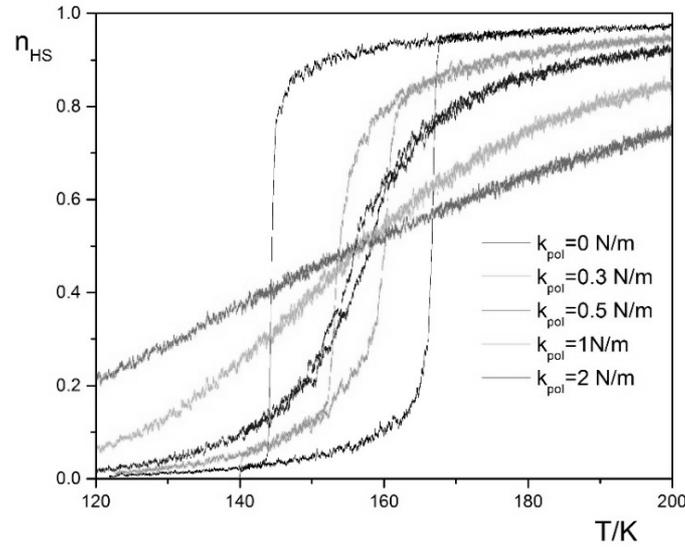


Fig. 4 – Thermal spin transition for a single spin crossover particle inside a matrix composed of molecules having the size as the average of HS and LS molecular sizes for various interactions between the sample and the matrix: larger interactions with the polymer decrease the cooperativity and determine a smoother transition, but the average transition temperature does not change.

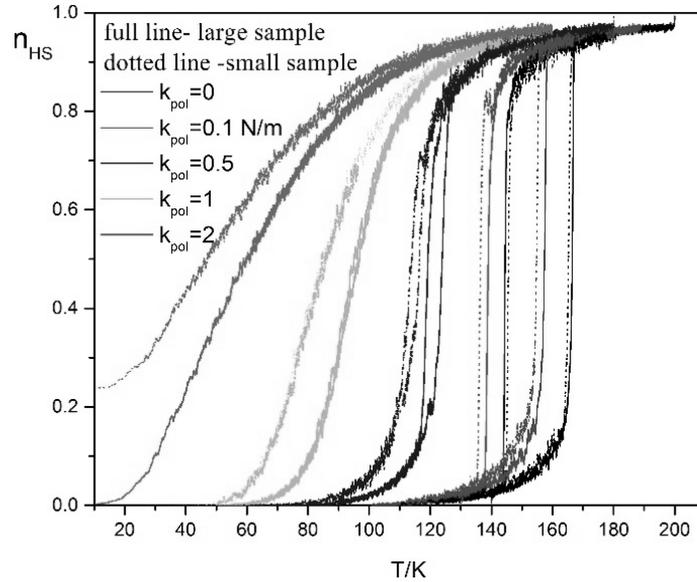


Fig. 5 – Thermal spin transition for a single spin crossover particle inside a matrix composed of molecules with molecular size equal to HS molecular sizes for various interactions between the sample and the matrix and for two sizes of spin crossover nanoparticle (1251 and 2691 molecules): larger interactions with the matrix shift the transition towards a lower temperature, decrease the cooperativity and determines a smoother transition. The effects are more preminent for the smaller sample.

In the second case, the transition temperature is shifted towards lower values as the k_{pol} increases and for larger k_{pol} , it becomes incomplete (Fig. 5). We have considered two sizes of spin crossover particles and we found that the shift is larger as the sample is smaller, which corresponds to experimental data for spin

crossover nanoparticles. Therefore the main drawback of the model with a simple shell of neutral molecules around the spin crossover particle is eliminated here when considering a full matrix embedding the spin crossover particle. As the results for the system embedded in a matrix composed of molecules with size similar to HS spin crossover molecules are closer to experimental data, we shall refer further only to these systems.

In order to establish to which extent the change of one single spin crossover particle is transmitted through the matrix to other spin crossover particles, and, consequently influences their own transitions, we have considered several spin crossover particles inside a larger lattice of surrounding matrix neutral molecules. Every spin crossover particle is composed by 1251 molecules, while the other parameters are those specified previously. Thermal transitions for systems composed by four spin crossover particles, together with a comparison for a single spin crossover particle with the same size are presented in Fig. 6. One should notice that the presence of several spin crossover particles in the same matrix leads to a larger hysteresis loop – a sign of a larger cooperativity, while the temperature is shifted towards higher values. In other words, even if the spin crossover particles are separated by the flexible matrix, their behaviour is close to that of aggregated molecules.

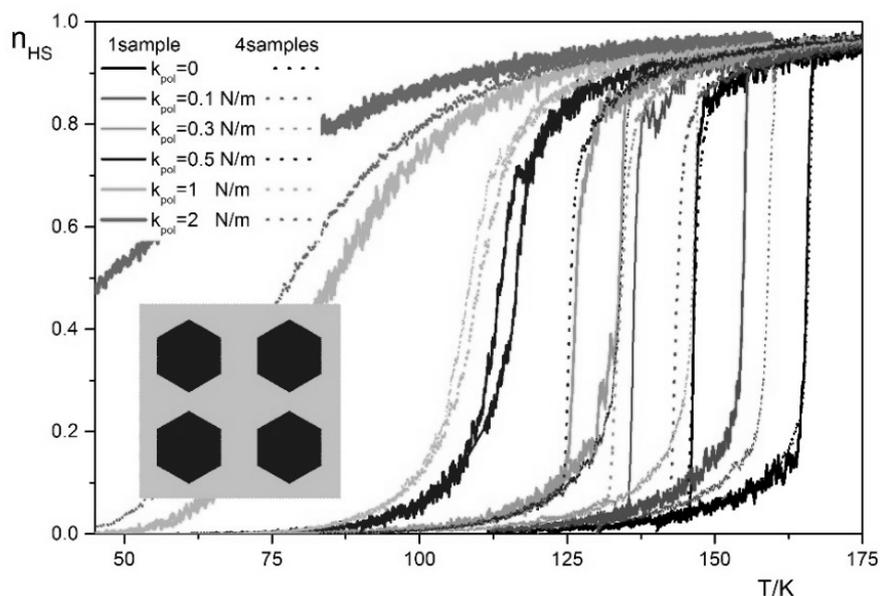


Fig. 6 – Thermal transition for one (full lines) or four (dotted lines) similar spin crossover particles situated inside the same matrix for different values of the matrix-spin crossover particle spring constant.

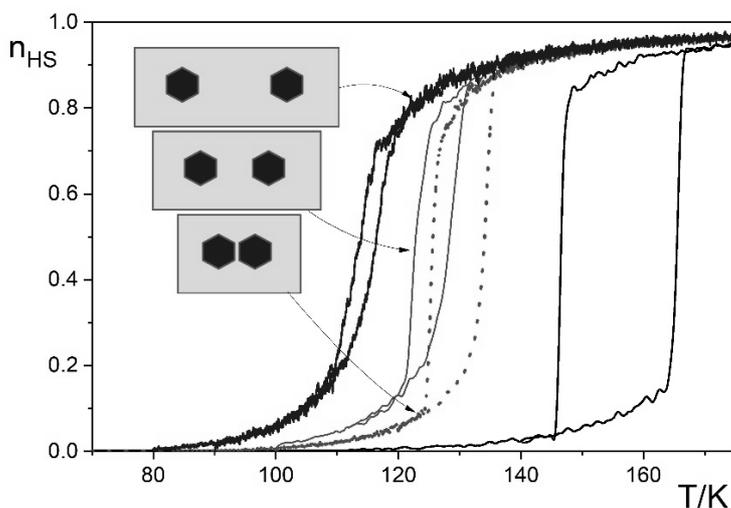


Fig. 7 – Thermal transition for spin crossover particles as a function of interparticle distance and comparison with the thermal transition for bulk (full black line).

In Fig. 7, we represent the effect of the distance between spin crossover particles on the transition temperature. The effect of reducing the distance between spin crossover particles is similar with the increasing the number of particles: the hysteresis becomes larger and shifts towards higher temperatures, approaching the hysteresis observed for larger samples or aggregated particles (bulk).

A further discussion concerns the microscopic processes (clustering and nucleation) observed during the thermal transition. Previous studies have shown that nucleation in spin crossover compounds starts from edges or corners in both experiments and elastic models applied to open boundary systems, while in Ising-like models and elastic models applied to periodical boundary systems, the nucleation starts from anywhere inside the bulk [17]. In Fig. 8, we present snapshots of a system composed by two spin crossover particles situated in an embedding matrix. One may notice that the nucleation starts for both systems at the edges that are face to face and closest to each other. In other words, the transformation of one particle is reproduced in the other almost like in a mirror and the matrix is actually coupling the particles.

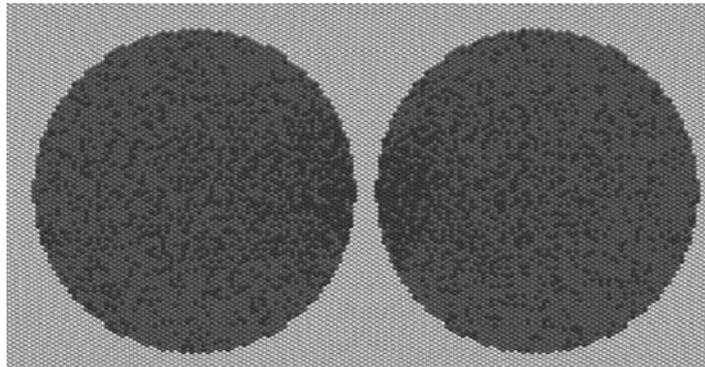


Fig. 8 – Snapshot of two spin crossover molecules, showing their reciprocal influence mediated by the matrix.

The results presented in Figs. 6–8 outline the role of the matrix in transmitting the information from one spin crossover particle to others. In order to understand the microscopic mechanism that facilitates this propagation, we show in Fig. 9 the local pressure on the matrix molecules just after the transition has started (a) and in the middle of the transition, where the distortions produced by the size difference of molecules in HS and LS states are the highest (b). The local pressure corresponds to the amplitude of elastic waves produced by the distortions determined by the different sizes of HS and LS molecules. At the beginning of the transition, the local pressures are smaller, but they dramatically increase during the transition, together with the coupling between the two molecules.

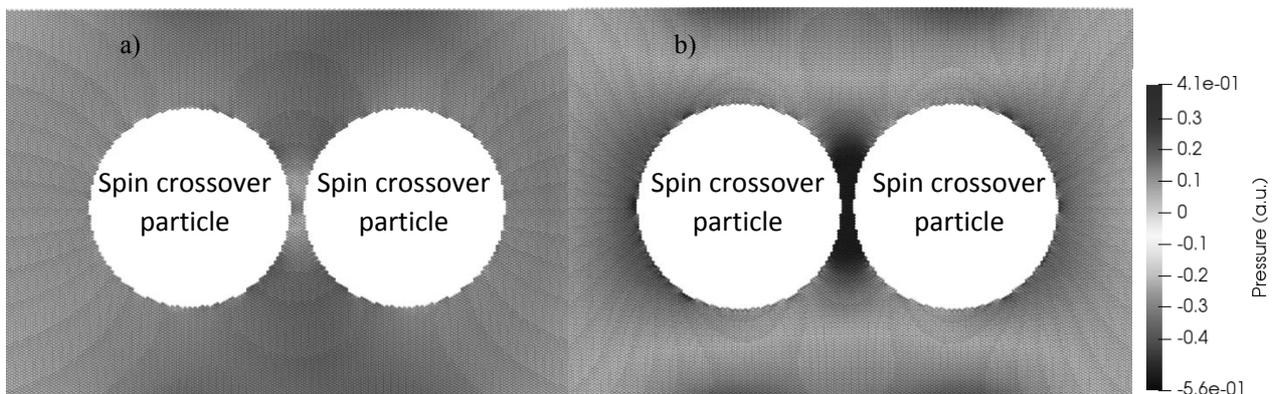


Fig. 9 – Local pressure on the matrix molecules, showing the elastic waves that facilitate the propagation of the information from one particle to another. a) at the beginning of the transition; b) in the middle of the transition. Color scale: blue: low local pressure, red: high local pressure. The molecules from spin crossover particles are omitted.

These results lead to the possibility to remote control spin crossover compounds. If, for example, we photoexcite a spin crossover particle situated inside a matrix, the information concerning the change of the

state will be transmitted by the matrix to the other spin crossover particles, which may also change their states, without a direct interaction with the environment.

3. CONCLUSIONS

In this paper we have successfully reproduced thermal transition curves corresponding to spin crossover nanoparticles embedded in matrices and we have discussed how the switches inside a spin crossover particle propagates through the lattice towards other spin crossover particles. In addition, we have studied how the density of spin crossover particles affects the transition curves, showing that the decrease of distances between particles leads to a behaviour close to the bulk. Further studies should include the effect of shape – many spin crossover nanoparticles are needle shaped – and the case of 3D nanoparticles.

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