

NUCLEATION IN SPIN TRANSITION MOLECULAR MAGNETS: A PARALLEL BETWEEN ISING-LIKE AND MECHANOELASTIC MODELS

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Abstract. In this paper we investigate the nucleation during the high-spin–low-spin relaxation in spin crossover solids in the framework of a Monte Carlo approach of Ising and mechanoelastic models in order to compare the results with experimental data. We also investigate the domain interface propagation through lattices with various boundary conditions, sizes, and structures. We show that, even they are very similar when reproducing macroscopic curves, the two models show different nucleation behaviors.

Key words: spin transition, Monte Carlo simulation, nucleation.

1. INTRODUCTION

In recent years, information technology has evolved significantly, requiring higher computing power and increased storage capacity. In this context, a potential solution for increasing the recording media density is represented by the spin crossover molecular magnets [1]. These metal coordination compounds in the d^n configuration, with n between 4 and 7, situated in an octahedral ligand field, show a bistability between two states in thermodynamic competition: the diamagnetic low-spin state (LS) at low temperatures and the paramagnetic high-spin state (HS) at high temperatures, with different electronic, optical, magnetic, and volume properties. The spin transition process can be controlled by the amendment of internal parameters or by applying external perturbations such as temperature, pressure, field, light.

Both unit cell volume and bond-length are considerably larger for the HS state resulting, in addition, to a larger electronic degeneracy for this state. The change of molecular volumes during the transition is at the origin of elastic interactions and cooperativity, which, if strong enough, are responsible, at macroscopic scale, for the first-order transition, accompanying bistability, and hysteresis phenomena. At microscopic scale, elastic interactions induce nucleation, cluster formation, and growth of like-spin domains, i.e. domains of molecules in the same spin state. The role of clusters in the spin transition has been intensively studied in the last years, both from an experimental and a theoretical point of view [1].

Besides thermal transition, the effect of elastic interactions and clusters can be eloquently observed during the relaxation phenomena. If one irradiates the LS compound at low temperature with an electromagnetic radiation with an appropriate wavelength, the molecules will progressively commute to the HS metastable state (Light Induced Excited Spin State Trapping Effect) [2]. Subsequently, if the source of light is removed, the system relaxes towards fundamental level; this process is called relaxation in dark. The relaxation time can vary from nanosecond scale and even faster to days or months, depending on the actual temperature and type of compound. The relaxation curve can be single exponential, if interactions are small or sigmoidal and even steeper in the case of large enough elastic interactions. While in the first situation, the molecules flip randomly, in this second case, the individual spin change is influenced by the switching of the neighbouring molecules and therefore clusters of the same spin state molecules are produced. In Fig. 1 we present a typical sigmoidal relaxation curve together with the electronic state of HS and LS molecules. In order to quantitatively characterize the evolution of the system, one uses the so-called HS fraction, denoted n_{HS} , which represents the proportion of molecules in the HS state.

In this paper we discuss the evolution of clusters in the framework of two models in spin crossover compound: the classical Ising-like model and the more recent mechanoelastic model for different shapes and internal configurations of lattices. The paper is structured as following: first we present some relevant experimental data, then we introduce the principles of the two models and in the main part of the paper we discuss the evolution of clusters in the case of both models during the HS-LS relaxation in dark.

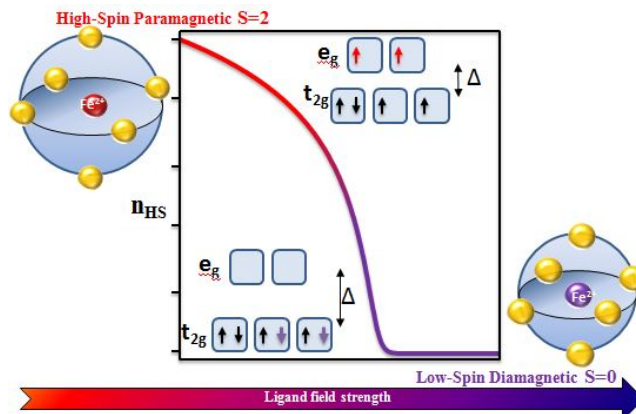


Fig. 1 – Electronic structure of the Fe atom in its $3d^6$ configuration for HS (up) and LS (down) states. Δ is the energy difference between e_g and t_{2g} orbitals, resulting from d orbitals due to the action of the octahedral ligand field. A typical sigmoidal relaxation curve for a cooperative compound (middle).

2. EXPERIMENTAL EVIDENCES

Convenient n_{HS} measurements are based on physical quantities (magnetic susceptibility, metal–ligand distance, specific heat) or spectroscopic data (optical absorption, diffuse reflectance, Mössbauer, Raman), which can be accurately determined in the HS and LS states. The spatiotemporal aspects of the spin transition were only recently considered, so far by means of optical microscopy [3, 4], which clearly showed the propagation of a phase boundary. Such experimental information promoted modelling work aiming to determine the location of nucleation centres at the thermal and photo-induced transitions, or to establish scaling laws for the light-induced phase separation.

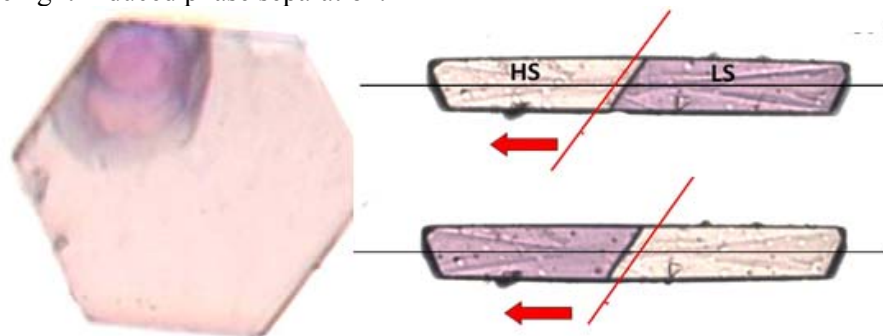


Fig. 2 – Experimental cluster evolution for a hexagonal sample of $[\text{Fe}(\text{bbtr})_3](\text{ClO}_4)_2$ during cooling down (HS-LS transition) (left) (adapted from [5]) and for a rectangular sample of $\text{Fe}(\text{NCSe})(\text{py})_2(\text{m-pypz})$ during cooling down (right up) and heating up (right down) (adapted from [6]).

In a pioneering work, Chong *et al.* [5] have investigated the thermal spin transition in single crystals of $[\text{Fe}(\text{bbtr})_3](\text{ClO}_4)_2$ ($\text{bbtr} = 1,4\text{-di}(1, 2, 3\text{-triazol-1-yl}) \text{ butane}$) using the optical microscopy technique. The growth of the low-spin phase was observed for different crystal orientations and sizes. Their results show that the process always starts from a corner of the crystal but its further development depends on the size, shape, and thermal history of the crystal (Fig. 2 left). In crystals of smaller size, under isothermal conditions, the low-spin phase develops in a continuous way through the propagation of a rather well defined transformation front, with a higher propagation velocity inside the planes perpendicular to the c axis. In

larger crystals, the spontaneous occurrence of inhomogeneous stresses led to a stepwise propagation process. In addition, size effects associated with the onset of inhomogeneous stresses in the crystals, lead to mechanical instability in the case of larger crystals. The propagation velocity of the interface (Fig. 2 right) was then determined and its anisotropic character revealed (slower along the packing direction of the 2D polymeric planes). The stepwise isothermal relaxation reported in [7] was assigned to crystal aging due to the development of inhomogeneous stresses at the transition. In the following, we shall undertake the detailed investigation of the spatiotemporal aspects, in order to document the fascinating problem of the mechanical instability and set up realistic models involving the rheological response of the materials.

3. MODELS

The simplest model to analyse spin crossover macroscopic behaviour is the mean field model, which implies random distribution of HS and LS species during the transition. However mean-field models do not distinguish between short and long range interactions and therefore do not allow an advanced analysis of the propagation of spin flipping inside the sample. In order to realize such an analysis, more complex models should be used. From a historical point of view, the first between these models was the Ising model [8, 9]. The Ising models to study SC complexes implies the introduction of short and long range intermolecular interactions between spin crossover units through an Ising-like Hamiltonian. It should be noted that these interactions are not from magnetic origin, but merely they are resulting from the bond length change accompanying every spin change. The Ising-like Hamiltonian has been first solved in mean-field approximation [8], while subsequent extensive studies have treated successfully the dynamic [10] and static properties [11] of SC compounds.

In this model, the two states of molecules have different degeneracies and a lower energy for the LS state. By associating a fictitious spin to each molecule ($\sigma_i = \pm 1$ for HS (LS) state) [12], the short-range interactions J and long-range interactions G can be written as exchange interactions in the Hamiltonian:

$$H = \frac{1}{2} \sum_i (D - k_B T \ln g) \sigma_i - J \sum_{i,j} \sigma_i \sigma_j - G \sum_i \sigma_i \langle \sigma \rangle, \quad (1)$$

with D and g the energy difference and the degeneracy ratio between the two states, k_B the Boltzmann constant, and T the temperature.

The high spin fraction can be expressed as a function of the “fictitious magnetization” $\langle \sigma \rangle$ as:

$$n_{HS} = \frac{1 + \langle \sigma \rangle}{2}. \quad (2)$$

While the short range interactions depend on shape and distance between neighbour molecules and can be correlated to the existence of covalent bonds, the long range interactions are purely of elastic nature and are mediated by the lattice [13]. Consequently, the intermolecular interactions play the role of an internal pressure in the Ising-like model and the effective interaction should be taken proportional to n_{HS} , the fraction of molecules in HS state. In addition, one should note the differences between this model and the classical Ising model: here the field ($D - k_B T \ln g$) is temperature dependent, so the results concerning critical temperatures do not have a correspondent for the present model.

As we have stated in the Introduction, due to the difference of molecular sizes between LS and HS states, the lattice will be distorted during the transition. The larger volume of HS molecules as compared to LS molecules induces elastic stresses in the crystalline network, thus changing the probability of other molecules to switch to the LS state with the decreasing of n_{HS} during HS-LS relaxation. Therefore, we have to assume that the intermolecular interactions themselves arise from stresses due to changes of the volume, shape, and elasticity of the lattice. This behaviour described as an “elastic interaction” between the molecules appears also as a total interaction that is the sum between an infinite range contribution, originating in lattice strains and a direct contribution from pair interaction.

Therefore, the Ising-like model have some limits as it keeps constant the intermolecular interactions and does not consider distortions. In order to correct this problem a new class of models – the elastic models – have been elaborated [14–16]. In these models, the short and long range interactions are replaced by purely elastic interactions. The molecules, considered as rigid spheres, are linked by springs, which can be compressed or elongated during the transition, resulting in practically an infinite number of possible interaction terms between molecules. The Hamiltonian for such an elastic model can be written as [17]:

$$H = \frac{1}{2} \sum_i (D - k_B T \ln g) \sigma_i + \frac{k}{2} \sum_{i,j} \delta x_{ij}^2, \quad (3)$$

where the first term corresponds to the classical Hamiltonian used to treat the spin-crossover Ising-type system and the second term stands for the elastic energy, calculated as the sum of energies for all the springs in the system, with k the elastic spring constant and δx_{ij} the individual spring elongations between all neighboring molecules in the system. In this work, we shall use the mechanoelastic model, which implies that after every switching the new position of molecules are calculated, by solving systems of differential equations, in order to reach the mechanical equilibrium.

Our aim is to investigate to what extent the Ising-like model still gives satisfactory results and when it should be replaced by one of the more complex elastic models. For the sake of simplicity here we shall study the clustering phenomena during the HS-LS relaxation for both models, which implies that the clusters will be produced at the same temperature for all simulations (here we considered 60 K). The evolution of the system will be discussed through a Monte Carlo Arrhenius dynamics, in which the transition probabilities are modulated by an activation energy barrier E_a . In this approach, the transition probabilities can be written [18, 19]:

$$P_{HS \rightarrow LS}^i = \frac{1}{\tau} \exp\left(\frac{D - k_B T \ln g}{2k_B T}\right) \exp\left(-\frac{E_a + 2G\langle\sigma\rangle + 2J\sum\sigma_{neighbors}}{k_B T}\right) \quad (4a)$$

$$P_{LS \rightarrow HS}^i = \frac{1}{\tau} \exp\left(-\frac{D - k_B T \ln g}{2k_B T}\right) \exp\left(-\frac{E - 2G\langle\sigma\rangle - 2J\sum\sigma_{neighbors}}{k_B T}\right) \quad (4b)$$

in the framework of an Ising-like model and [20]:

$$P_{HS \rightarrow LS}^i = \frac{1}{\tau} \exp\left(\frac{D - k_B T \ln g}{2k_B T}\right) \exp\left(-\frac{E_a + \kappa p_i}{k_B T}\right) \quad (5a)$$

$$P_{LS \rightarrow HS}^i = \frac{1}{\tau} \exp\left(-\frac{D - k_B T \ln g}{2k_B T}\right) \exp\left(-\frac{E_a - \kappa p_i}{k_B T}\right) \quad (5b)$$

in the framework of the mechanoelastic model, where τ is a scaling constant, chosen so that the above probabilities are well below unity at any temperature, κ is a scaling factor between the local pressure and the activation energy of the individual molecule, and p_i is the local pressure acting on molecule i , defined as $p_i = \sum_{\text{neighbours springs}} k \cdot \delta x_{ij}$, with δx_{ij} taken positive for elongated springs and negative for compressed ones. If the

springs near a HS molecule are elongated in the mechanoelastic case or most of neighbours are already in the LS state, the probability that this molecule passes to the bigger volume LS state is higher.

The simulation procedure is the following: (i) at the beginning we consider first of all the molecules are in the HS state (either the LS or the HS state); (ii) one calculates the transition probabilities (4) or (5) for a random molecule in the system; (iii) one generates a random number $r \in (0,1)$; if this number is smaller than the transition probabilities then the switch is accepted and the molecules flips to the new state; otherwise the molecule keeps it previous state; (iv) one repeats the steps (ii–iii) for all molecules in the system; when this step is finished we have realized a Monte Carlo step; (v) one updates the state of the system. While in the

Ising-like system, updating means only the spin changes, in the mechanoelastic model we have to update both the spin and the position of molecules. In this case, the switch of a molecule is accompanied by a change of its volume and an instantaneous forces will appear inside neighbouring springs, determining at first the shift in position of neighbour molecules and then progressively of all other molecules in the system. The molecules stop moving when all of them are in mechanical equilibrium, i.e. the resulting force on every molecule is zero; (vi) one repeats the step (ii–v) until all molecules have switched to LS state.

4. RESULTS

We have applied the Ising-like model and the mechanoelastic model for different system shapes and internal configurations (see Fig. 3). The “natural” 2D configurations (which are usually considered in simulations) of Ising-like and mechanoelastic models are respectively rectangular (every bulk molecule has four closest neighbours, within a rectangular lattice) and triangular (every bulk molecule has six closest neighbours within rectangular or hexagonal lattices). In addition, rectangular Ising lattices can be periodic (border molecules have opposite border molecules as closest neighbours) or open boundaries (border molecules have fewer neighbours than bulk ones). In order to realize an accurate comparison between the two models, we have considered not only rectangular Ising lattices, but also triangular Ising lattice for fitting with classical mechanoelastic lattice (for stability reasons the mechanoelastic should be hexagonal in the case of using a single elastic constant).

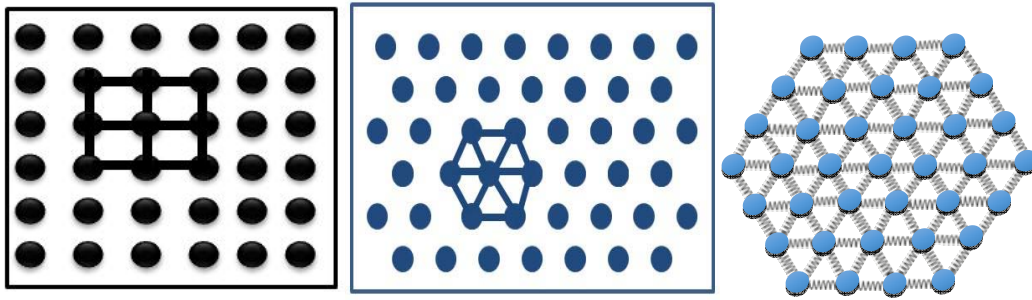


Fig. 3 – (Left) Ising rectangular lattice, (center) ising triangular lattice, (right) mechanoelastic triangular lattice.

First we have checked the differences between systems with periodic or open boundary conditions. For all the simulations presented below, the intrinsic parameters are $E_a = 400$ K, $D = 1470$ K, $k_B = 1$, $g = 1096$, $T = 125$ K, which correspond to the common experimental parameter values. In Fig. 4 we have represented HS-LS relaxation curves obtained for periodic and open boundary systems composed by 55296 molecules, with average and large short-range interactions together with snapshots of the evolution of the system at $n_{HS} = 0.8$. A fast analysis of the snapshots shows that nucleation appears both in open and periodic boundary conditions, with larger clusters in the case of larger short-range interactions. However, if in the case of periodic conditions, nucleation starts usually from bulk, open boundary conditions tend to favor the growth of clusters from edges. The first situation is different from what was experimentally observed, so we can conclude that the use of open boundary conditions is essential for obtaining clusters starting from edges. Therefore in the following discussion we shall refer only to open boundary systems. The comparison of relaxation curves in both boundary conditions does not reveal important differences: while in the case of smaller short-range interactions the relaxation curves are practically identical, the open boundary system relaxation seems somewhat faster due to a higher probability to switch for border molecules (and to several cluster formed), but their shape stays essentially the same. Consequently, the differences are merely at microscopic scale than at macroscopic scale.

Figure 5 deals with triangular structures of Ising and Mechanoelastic models for rectangular and hexagonal lattices. Similar to rectangular structures, Ising-like triangular structures determine the building-up of clusters starting from edges in both rectangular and hexagonal shapes. For large values of the short range intermolecular interaction parameter J , the nucleation starts only from edges; if the value of J decreases

then some clusters can be also observed inside the lattice. As previously observed in the framework of the mechanoelastic model the clustering start always from corners, results which are closer to experimental data [16]. The clustering from edges has been rarely observed, only at very low temperatures, when the probability for a molecule to switch from LS to HS state is very low [20]. Therefore, we can conclude that Ising-like model can be useful as a first approximation, but it cannot describe the exact experimental results. In addition, we have to observe that the relaxation curves look similar in all four situations – that is why both models can be successfully applied for the characterization of experimental relaxation (and thermal transition) curves, which are macroscopic in their intrinsic nature.

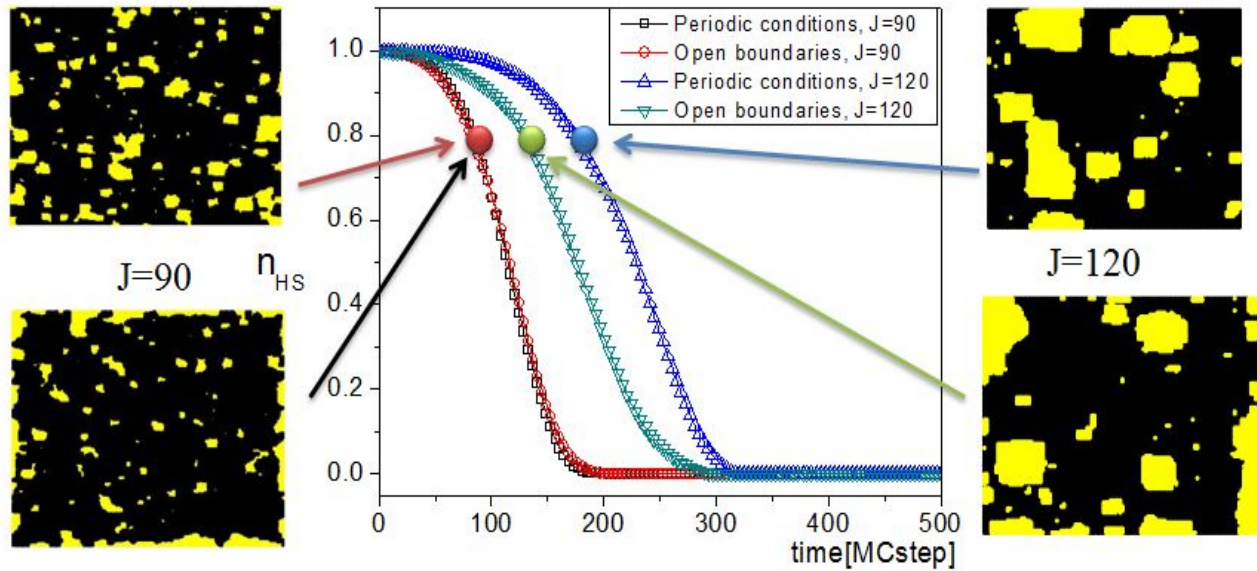


Fig. 4 – HS-LS relaxations for rectangular samples in rectangular configuration with different short range interaction terms for open and periodic boundary conditions (middle). Snapshots showing nucleation at $n_{HS} = 0.8$ for open boundaries (up) and periodic boundary conditions (down) for $J = 90K$ (left) and $J = 120K$ (right), $G = 10K$.

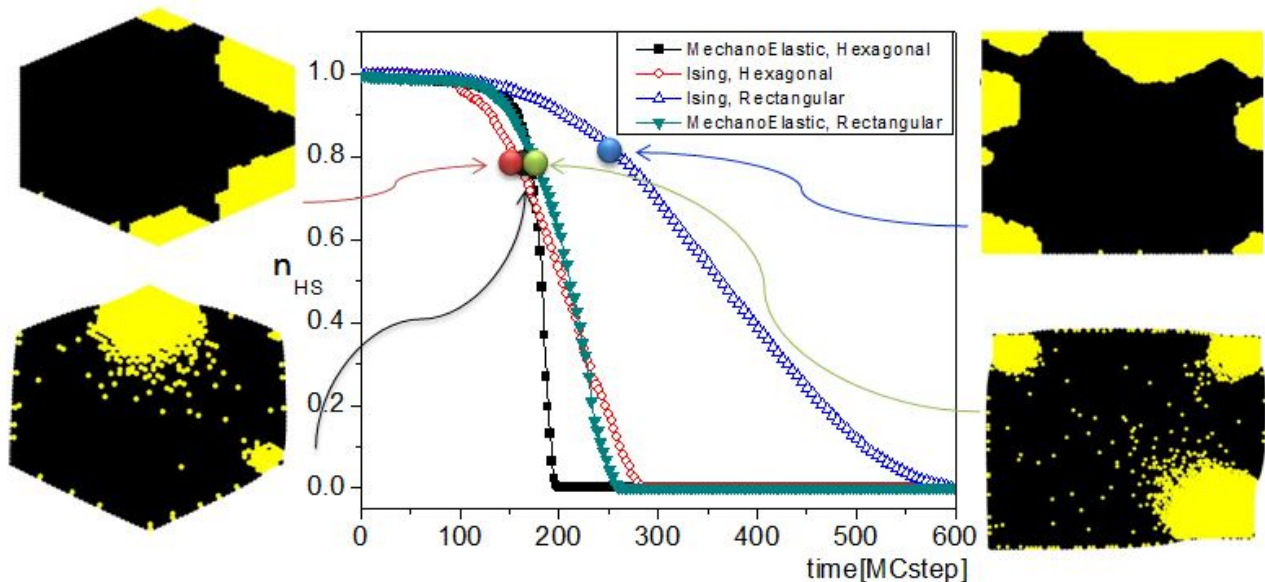


Fig. 5 – HS-LS relaxations for open boundary systems for system with hexagonal (11154 molecules) and rectangular (55225 molecules) shapes, in triangular configurations in the framework of Ising-like and mechanoelastic models. Snapshots of the system at $n_{HS} = 0.8$ for Ising systems with $J = 90K$, $G = 10K$ (up) and for mechanoelastic systems with $k = 600K$ (down).

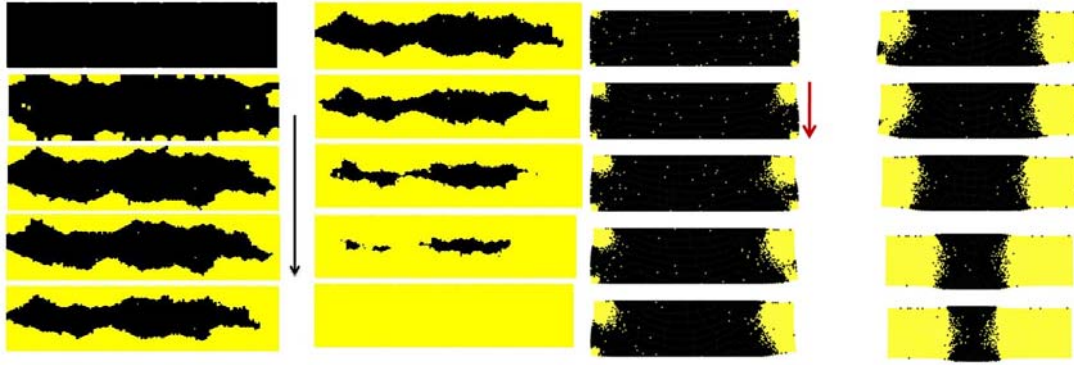


Fig. 6 – Cluster formation into a rectangle structure during relaxation process with a trigonal 2D lattice for an Ising-like system (the two columns at the left) and for a mechanoelastic system (the two columns at the right).

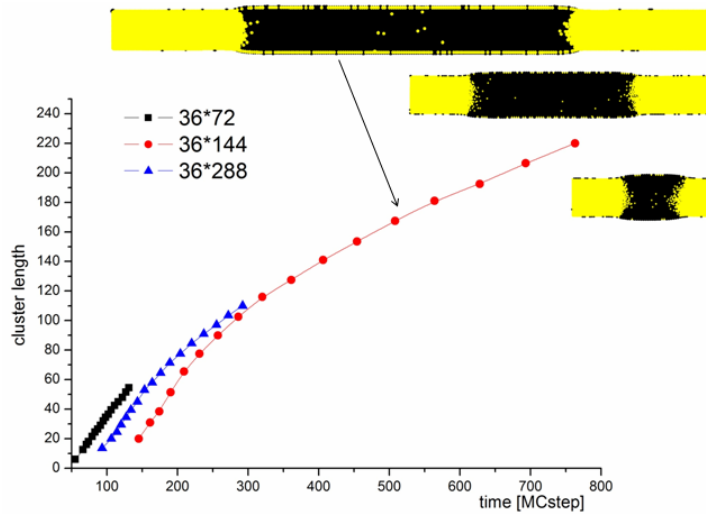


Fig. 7 – Cluster length evolution as a function of time for rectangular samples with different sizes.

In the following we shall address the problem of the propagation velocity of clusters, i.e. of the interface between the two phases. We choose rectangular systems with a large enough ratio between their length and their width, as we expect that the cluster will propagate along the larger side of the rectangle. In Fig. 6 we present snapshots during relaxation at the same temperature for rectangular systems with 11164 molecules in the framework of the Ising-like (left) and the mechanoelastic models (right). Excepting the interaction parameters, which are different due to the different nature of the models, all the other parameters are identical. The evolution of clusters in the two models is rather different: while in the mechanoelastic model the clusters start from extremities and then develop before joining towards the middle length, while keeping approximately a straight interface, in the Ising-like model, nucleation starts almost simultaneously from all the sides. Therefore it is not possible to define a propagation speed for the clusters in the Ising-like model, and we shall study the propagation velocity of the interface, only in the case of the Mechanoelastic model. Comparing with experimental data in Fig. 2 (right), one notices that for a rectangular shape, the difference between the clustering in the two models are dramatic.

In Fig. 7 we have represented the cluster length (calculated as a number of molecules on the edge belonging to the developing clusters by averaging the values from the left and the right clusters) as a function of the Monte Carlo step for different length/width ratios of a rectangular lattice, defining in this way the propagation velocity of the interface. It is worth noticing that for most of the time and for all samples, the propagation velocity is linear, similar with experimental data, as in Ref. [6]. A change in velocity appears in the case of the very long sample, where the velocity is larger at short times and then decreases. In addition, at short times, the speed seems to be similar regardless the size of the sample. We can conclude then that the velocity of the interface is a universal characteristic and depends only on the intrinsic properties of the sample (elastic constant, temperature), while it does not depend on the length/width ratio of the lattice.

5. CONCLUSIONS

In this paper we have compared the cluster development in 2D spin crossover compound in the framework of Ising-like and mechanoelastic model. We have found that even if the macroscopic relaxation curves have the same appearance, the clusters develop in different manners in open boundary lattices: from edges and from inside in the case of Ising-like model and from corners in the case of mechanoelastic model. These results may exceed the field of spin crossover materials and are important for any other material showing two phases with different volumes. Further studies will be devoted to the case of 3D lattices and to the study of clusters in spin crossover nanoparticles, as a function of sizes and shapes.

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REFERENCES

1. M. A. HALCROW (ed.), *Spin-crossover materials-properties and applications*, John Wiley & Sons: Chichester, UK, 2013.
2. A. HAUSER, *Light-induced spin crossover and the high-spin→low-spin relaxation*, in: *Spin crossover in transition metal compounds II*. Top. Curr. Chem., **234**, pp. 155–198, 2004.
3. A. GOUJON *et al.*, *Neutron Laue diffraction on the spin crossover crystal [Fe(1-n-propyltetrazole)6](BF₄)₂ showing continuous photoinduced transformation*, Phys. Rev. B, **73**, 104413, 2006.
4. C. CHONG, F. VARRET, K. BOUKHEDDADEN, *Electronic and structural aspects of spin transitions observed by optical microscopy. The case of [Fe(ptz)₆](BF₄)₂*, J. Phys. Chem. B, **114**, pp. 1975–1984, 2010.
5. C. CHONG *et al.*, *The kinetics features of a thermal spin transition characterized by optical microscopy on the example of [Fe(bbtr)₃](ClO₄)₂ single crystals: size effect and mechanical instability*, Chem. Phys. Lett., **504**, pp. 29–33, 2011.
6. A. SLIMANI *et al.*, *Velocity of the High-Spin Low-Spin Interface Inside the Thermal Hysteresis Loop of a Spin-Crossover Crystal, via Photothermal Control of the Interface Motion*, Phys. Rev. Lett., **110**, 087208, 2013.
7. I. KRIVOKAPIC, C. ENACHESCU, R. BRONISZ, A. HAUSER, Chem. Phys. Lett., **455**, pp. 192–196, 2008.
8. A. BOUSSEKSOU *et al.*, *Ising-like model for the two-step spin-crossover*, J. Phys. I, **2**, pp. 1381–1403, 1992.
9. F. VARRET *et al.*, *The Ising-like model applied to switchable inorganic solids: discussion of the static properties*, C. R. Chim., **6**, pp. 385–393, 2003.
10. K. BOUKHEDDADEN, I. SHTETO, B. HÔO, F. VARRET, *Dynamical model for spin-crossover solids. I. Relaxation effects in the mean-field approach*, Phys. Rev. B, **62**, pp. 14796–14805, 2000.
11. B. HOO, K. BOUKHEDDADEN, F. VARRET, *Two-variable macroscopic model for spin-crossover solids: Static and dynamic effects of the correlations*, Eur. Phys. J. B, **17**, p. 449–457, 2000.
12. J. WAJNFLASZ, R. PICK, *Low-spin-high-spin transitions in Fe²⁺ complexes*, J. Phys. (France), **32**, pp. C1-91-C1-92, 1971.
13. H. SPIERING, N. WILLENBACHER, *Elastic interaction of high-spin and low-spin complex molecules in spin-crossover compounds. II*, J. Phys. Condens. Matter, **1**, pp. 10089–10105, 1989.
14. Y. KONISHI, H. TOKORO, M. NISHINO, S. MIYASHITA, *Monte Carlo simulation of pressure-induced phase transitions in spin-crossover material*, Phys. Rev. Lett., **100**, 067206, 2008.
15. M. NISHINO, C. ENACHESCU, S. MIYASHITA, P.A. RIKVOLD, K. BOUKHEDDADEN, F. VARRET, *Macroscopic nucleation phenomena in continuum media with long-range interactions*, Sci. Rep., **1**, 162, 2011.
16. C. ENACHESCU, L. STOLERIU, A. STANCU, A. HAUSER, *Model for Elastic Relaxation Phenomena in Finite 2D Hexagonal Molecular Lattices*, Phys. Rev. Lett., **102**, 257204, 2009.
17. C. ENACHESCU, M. NISHINO, S. MIYASHITA, A. HAUSER, A. STANCU, L. STOLERIU, *Monte Carlo Metropolis study of cluster evolution in spin-crossover solids within the framework of a mechanoelastic model*, Phys. Rev. B, **86**, 054114, 2012.
18. A. DOBRINESCU, C. ENACHESCU, A. STANCU, *Ising-like model study of size dependence relaxation in spin crossover complexes*, J. Magn. Magn. Mater., **321**, pp. 4132–4138, 2009.
19. A. ATITOAIE, R. TANASA, C. ENACHESCU, *Size dependent thermal hysteresis in spin crossover nanoparticles reflected within a Monte Carlo based Ising-like mode*, J. Magn. Magn. Mater., **324**, pp. 1596–1600, 2012.
20. C. ENACHESCU, M. NISHINO, S. MIYASHITA, K. BOUKHEDDADEN, F. VARRET, P.A. RIKVOLD, *Shape effects on the cluster spreading process of spin-crossover compounds analyzed within an elastic model with Eden and Kawasaki dynamics*, Phys. Rev. B, **91**, 104102, 2015.

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