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Model for Elastic Relaxation Phenomena in Finite 2D Hexagonal Molecular Lattices

Cristian Enachescu,* Laurentiu Stoleriu, and Alexandru Stancu
Department of Physics, Alexandru Ioan Cuza University, Iasi, Romania

Andreas Hauser
Département de Chimie Physique, Université de Genève, Switzerland

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The relaxation in a spin transition compound is modeled on the basis of molecules interacting by the way of connecting springs and situated in a bidimensional open boundary hexagonal lattice. The switch of individual molecules is randomly checked using a standard Monte Carlo procedure. The switching probability depends on the energy gap between the two states in the absence of interactions and on the elongations of the nearest springs. The main characteristics of the experimental relaxation curves are reproduced and clustering and nucleation phenomena are detected.

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As a consequence of the foreseeable future limitation of the recording densities in magnetic media [1], new types of switchable materials such as molecular magnets are now being intensely investigated. However, they are generally affected by strong quantum effects, in conflict with the deterministic character of recording [2,3].

Other potential recording media of the future are the spin-crossover solids that can be switched between two states in thermodynamic competition: the diamagnetic (LS) low spin state and the paramagnetic high spin (HS) state, using a range of physical perturbations such as temperature, pressure or electromagnetic radiation. These features made them candidates for a fully optical memory device, triggering an avalanche of studies with remarkable recent results of compounds that can be switched at room temperature [4], the production of spin-crossover nanoparticles [5] and the first optical switches between the two stable states of the material [6]. The transition between the two states is accompanied by changes in magnetic and optical properties as well as in the unit cell volume. By light irradiation using appropriate wavelengths, the LS ground state at low temperature can be switched to the metastable HS state. After switching off the light, the metastable state relaxes back to the stable LS state by a nonradiative process. The measured output variable of the system is the proportion of spin-crossover units in the HS state, denoted here as n_{HS}.

To understand this complex behavior, several theoretical models have been elaborated in the past, involving short- and long-range interactions arising from stresses due to the metal-ligand bond length changes and to the simultaneous change in volume of the molecules as well as of the whole crystal during the transition [7]. Ising-like models have been partially successful in explaining several aspects of cooperative behavior [8–10]. The elastic interactions are seen as an internal pressure in these models, and consequently the effective interaction is proportional to the fraction of molecules in HS state. In contrast, the DOMINO effect [11] points to local statistically distributed changes causing a global structural change. Recently, several papers proposed elastic models based on a ball and string concept (i) for a linear chain described by an atom-phonon coupling model [12], (ii) for two-dimensional systems using molecular dynamics [13], and (iii) for 3D systems using Monte Carlo Metropolis methods [14]. In a recent paper, we simulated hysteresis loops for a system of molecules in a finite 2D hexagonal lattice connected by springs and subjected to external pressure [15], thereby considering distributions of transition temperatures similar to the Preisach model [16] as suggested by the FORC diagram method [17].

Here we present a simple model for studying the relaxation behavior of the metastable HS state at low temperatures and clustering phenomena in open boundary systems. We consider the spin-active units to be rigid spheres situated in a hexagonal 2D lattice, in which each unit has six nearest neighbors and interacts with them by the way of elastic connecting springs (Fig. 1). As will become evident, this model offers physical support for both short and long-range interactions [9]. The spin-active units might be seen not only as individual molecules, but also in the larger sense of interacting domains. However, for simplicity, in the following the term ‘‘spin-active unit’’ will refer essentially to individual molecules.

In the initial state of the system, all the molecules are in the metastable HS state and no external pressure is applied to the system. Consequently, all the springs are unstressed and no local pressure acts on molecules. Then, an external pressure p, simulated by forces acting on the particles situated at the edge of the system, is applied to the network. These forces are taken to be of equal absolute value and oriented in the direction of the springs connecting the particle with its neighbors inside the lattice (Fig. 1). The external pressure produces a compression of all springs in the systems, until the vector sum of the forces acting on all molecules becomes zero. This approach ensures that, when

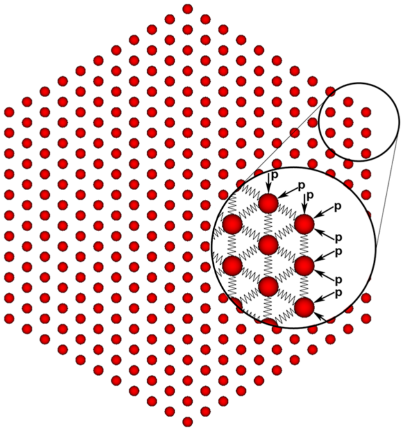

FIG. 1 (color online). The hexagonal network of particles connected with springs.

the system reaches the equilibrium, the local pressure is the same for all particles:

$$p_i = \sum_{\text{closest springs}} k\delta l_i + \sum_{\text{missing springs}} p \tag{1}$$

with k the spring constant, δl_i the elongations of the closest springs (taken positive if compressed, negative if elongated). The second term is considered only for edge molecules.

The simulation starts by randomly choosing a site in the system and verifying if it flips from the HS to LS state. The probability for switching between the HS and LS states depends on the temperature and the local pressure on a given molecule in a given state, according to the classical activation formula presented in [18]:

$$P_i = k_0 \exp\left(-\frac{E - \kappa p_i}{T}\right), \tag{2}$$

where k_0 is a preexponential factor, E is the activation energy in the absence of interactions, which is therefore the same for all molecules, T is the temperature, p_i the pressure force acting on the ith molecule and κ a constant that establishes to which extent the local pressure influences the relaxation probability. We calculate the switching probability using Eq. (2) for every molecule and then generate a random number, η. If this number is smaller than the probability, the molecule switches from HS to LS, otherwise it stays in the HS state. A Monte Carlo time step is concluded when all molecules in the system have been interrogated once.

When a molecule switches from HS to LS, the instantaneous force acting on it will determine at first the shift in position of nearest neighbors and then progressively of all the other molecules. A 2% difference between the diameters of a molecule in the HS state and the LS state was taken as model value. To find the equilibrium positions for all molecules in the system, we consider that every molecule has a damped oscillatory-type motion, and we solve iteratively the following system of coupled differential equations:

$$m\frac{d^2x_i}{dt^2} = F_{xi} - \mu\frac{dx_i}{dt} \qquad m\frac{d^2y_i}{dt^2} = F_{yi} - \mu\frac{dy_i}{dt} \tag{3}$$

until the maximum change in position of any molecule between two consecutive steps is smaller than a chosen parameter (less than 0.1%).

The following notations have been used: x_i, y_i are the Cartesian coordinates of molecule i, μ is the damping constant, and F_{xi}, F_{yi} are the algebraic sums of forces acting on particle i in the two directions, given by

$$F_{xi} = \sum_{\text{all}} k\delta l_{x,i} + p_x, \qquad F_{yi} = \sum_{\text{all}} k\delta l_{y,i} + p_y \tag{4}$$

with $\delta l_{x,i}$, $\delta l_{y,i}$ the components of elongation of every spring around the particle and p_x, p_y the external pressures forces on the two axes, taken into account only for edge particles. The system of equations is solved using the Gear's BDF method [19]. To simulate the full relaxation curve, the above procedure is continued until all the molecules have switched to the LS state.

In the simulations below, we have used hexagonal networks (Fig. 1) with 2791 molecules (30 molecules on each side of the hexagon). In contrast to rectangular lattices [13,14], the hexagonal lattice is inherently stable even with only nearest neighbor interactions, thus keeping the number of parameters at a minimum. There are several examples of spin-crossover compounds with hexagonal sheet layers [20].

We have simulated relaxation curves at various temperatures and different external pressures, assuming the elastic constants to be independent on these parameters in analogy to previous studies [21] [Fig. 2(b)]. The relaxation curves show the typical sigmoidal shape for a cooperative process [18], where the energy barrier progressively decreases while the relaxation proceeds. As in the thermally activated regime of real spin-crossover complexes, the relaxation is faster at higher temperature and for increasing pressures.

The simulations have also clarified a very complex phenomenon, essential in crystalline spin-crossover compounds—the cooperativity. To explain it, some authors claim that the elastic constant depends on the spin state

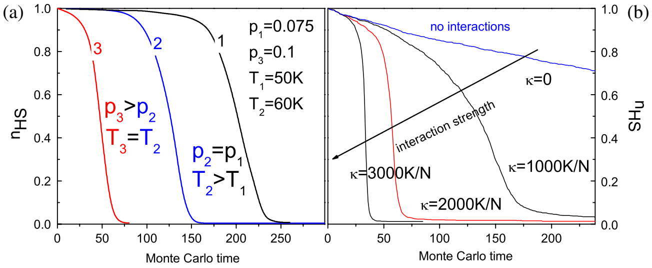

FIG. 2 (color online). Dependence of relaxation time on pressure and temperature (a); and on interaction strength (b). The following model values were used: $E = 450$ K, $k = 1$ N/m, $\mu = 0.5$ N · s/m, $k_0 = 1$.

[12] or temperature. Also, two different elastic constants for nearest neighbors and next nearest diagonal neighbors in square and cubic lattices had to be considered by other authors [13,14] to stabilize the square latices. In our model, we have used the same elastic constant for all the molecules in both spin states, and we still can reproduce the main experimental results.

In real systems, cooperativity is due to the large difference in metal-ligand bond lengths, and to corresponding differences in unit cell volumes between the two spin states. In our system when a molecule changes its state, the local distortions affect not only the nearest neighbors, but are causing an effective long-range interaction between all molecules in the system. In Fig. 3 we present two snapshots of the same system at two different moments during relaxation. We notice that for a small fraction of LS molecules (left panel), there are still a lot of HS molecules subjected to a constant or only weakly varying pressure. However, for a higher fraction of LS molecules (right panel) the pressure acting on them increases, in particular, in the vicinity of the LS molecules. According to Eq. (2), these molecules have a bigger probability to switch to the LS state than at the beginning of the relaxation process. Cooperative effects manifest themselves in cluster formation inside the lattice as the relaxation proceeds leading to the conclusion that the number of particles switching within a given time interval increases as more molecules populate the LS state.

An additional interesting aspect is the influence of the interaction strength on the relaxation curves. Interaction strength can be modified by changing the parameters κ or k with similar results. For weak interactions, as in the case of diluted crystals, the relaxation is single exponential. In strongly interacting systems, the relaxation curves become self-accelerated and increasingly steeper. This evolution is displayed in Fig. 2(b) for a fixed value of the relaxation rate constant at the beginning of the relaxation. As the interaction becomes stronger, the relaxation time decreases due to the cluster formation. Actually, for different interaction strengths the systems relax in rather different regimes. As expected, in the absence of interactions, the molecules pass from HS to LS independently of each other. For moderate values of the spring constant, some clusters form, but on average the HS and LS molecules are distributed randomly in the sample during the relaxation process [Fig. 4(a)]. This situation resembles the case where the elastic interactions are only of long-range nature. However, even for moderate interactions the buildup of correlations results in deviations from mean field behavior, in accordance with several experimental observations. If the spring constant is high enough then the clusters are bigger and develop faster throughout the sample, starting from edge or corner and leading to fluctuations, nucleation and growth phenomena. An infinite avalanche phenomenon [22] can be defined in such a case: when several molecules change their states, they will trigger their neighbors to flip resulting in a discontinuous jump in the HS fraction. Such a situation leads to nonrandom distributions of HS and LS molecules. [Fig. 4(b)]. In this case the deformations of the crystal are bigger and may lead to its collapse. Reference [20] provides an illustrative example of relaxation curves with a shape typical for a nucleation and growth mechanism and the formation of domains. Previously, domains have been experimentally observed during the thermal transition or photoexcitation [23]; a very recent study by optical microscopy at cryogenic temperatures shows that domains most often grow starting from a corner and present an evolution similar to our simulations [24]. Further experimental proofs could possibly be gained by elastic neutron or x-ray scattering experiments. We have tried to simulate the relaxation curves corresponding to two situations de-

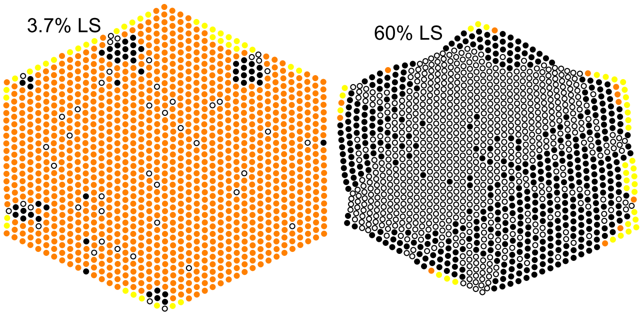

FIG. 3 (color online). Snapshots of a system with moderate interaction ($\kappa = 2000$ K/N) strength during relaxation. Open circles correspond to LS molecules; full circles correspond to HS molecules and are color coded according to the pressure acting on them: red circles indicate molecules with approximately the same pressure as at the beginning, molecules with a lower or higher pressure acting on them are indicated by yellow and black circles, respectively.

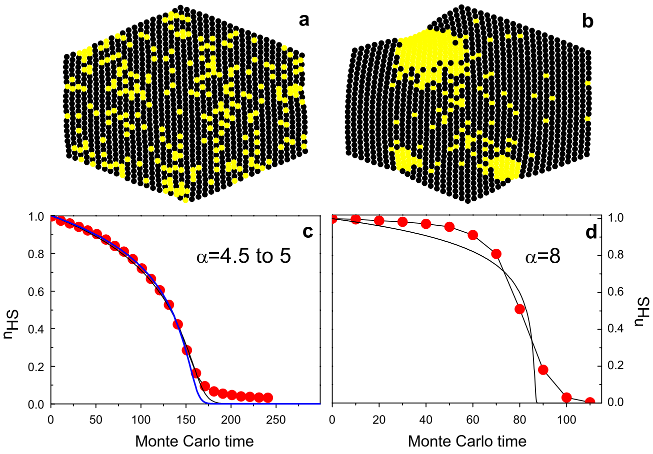

FIG. 4 (color online). Snapshots of spin configurations when around 10% of molecules are in the LS state showing the difference between the behavior observed for weak, $\kappa = 1000$ (a) and strong, $\kappa = 3000$ (b) interactions. Calculated relaxation curves and best fit with the classical mean field model (c) and (d). Yellow circles correspond to LS sites, black circles to HS sites.

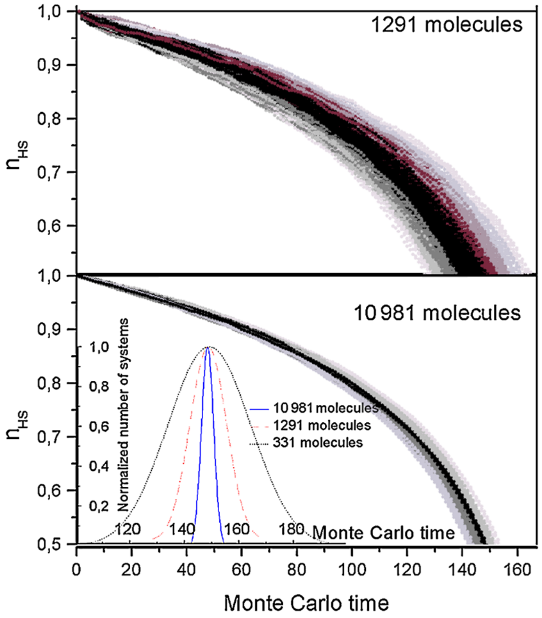

FIG. 5 (color online). First part of 1000 relaxation curves for a system with 1291 molecules (top) and 10 981 molecules (bottom). Darker parts indicate more relaxation curves in respective regions. Inset: distributions of relaxation times for different systems.

scribed using the macroscopic classical mean field model, where the internal pressure effect is taken into account by the way of the self-acceleration parameter α [25,26]. If the relaxation curves obtained for the weak interaction system can be easily simulated with a reasonable α value [Fig. 4(c)], this is not possible in the case of nucleation and avalanche phenomena [Fig. 4(d)].

Because our system does not rely on periodic boundary conditions, it is important to establish how much sample size influences the relaxation curves. Besides size effects, spatial fluctuations, not considered in the mean field equation, can lead to notable deviation of the relaxation curves from an average curve [27]. To study these finite size effects, we have calculated for the same system and under the same conditions, several relaxation curves, with different randomizations (various η random numbers). The distributions of relaxation times are presented in the inset of Fig. 5 for different system sizes. They are close to Gaussian, conform to the central limit theorem [28]. The width of the distribution tends to widen as the number of molecules decreases which suggests that the way cluster formation takes place inside the lattice influences the evolution of small systems. As the number of molecules increases, clustering becomes a statistical phenomenon, which leads to smaller fluctuations of the total switching time. Another representation of this variation is plotted in main Fig. 5.

In conclusion, we have modeled the HS → LS relaxation in a 2D hexagonal spin-crossover system by numerical simulation within the framework of an elastic model considering distortions determined by the volume change during the passage from HS to LS. We have considered only very simple assumptions, namely, a single elastic interaction constant between nearest neighbors. Nevertheless, all the typically observed phenomena in spin transition crystals can be simulated. In particular, the universal characteristics of nucleation and growth phenomena, shown to be determined by boundary effects, and the different regimes can be described within a unified model. The key of the present model lies in the inherent geometrical stability of the hexagonal lattice. This aspect should be taken over for instance in a future 3D model.

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*cristian.enachescu@uaic.ro

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