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Shape effects on the cluster spreading process of spin-crossover compounds analyzed within an elastic model with Eden and Kawasaki dynamics

Cristian Enachescu,[1,*] Masamichi Nishino,[2] Seiji Miyashita,[3] Kamel Boukheddaden,[4] François Varret,[4] and Per Arne Rikvold[5]
[1]*Faculty of Physics, Alexandru Ioan Cuza University, Iasi, 700506, Romania*
[2]*Computational Materials Science Center, National Institute for Materials Science, Tsukuba, Japan*
[3]*Department of Physics, The University of Tokyo, Tokyo, Japan*
[4]*Groupe d'Etude de la Matière Condensée, Université de Versailles, Versailles, France*
[5]*Department of Physics, Florida State University, Tallahassee, Florida, 32306-4350, USA*

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In this paper we study the growth properties of domains of low-spin molecules in a high-spin background in open-boundary elliptically shaped spin-crossover systems within the framework of a mechanoelastic model. The molecules are situated on a triangular lattice and are linked by springs, through which they interact. Elliptical shapes are chosen in order to allow an in-depth analysis of cluster shapes as a function of the local curvature at their starting point and the length of the interface between the two phases. In contrast to the case of rectangular and hexagonal shapes, where the clusters always start from corners, we find that for ellipses clusters nucleate from vertices, covertices, or any other site. We apply and compare two kinds of dynamics, Eden-like and Kawasaki, in order to determine the stable shape of the clusters and the most probable starting points. We show that the wetting angle for small clusters is somewhat higher than $\pi/2$ and approaches this value only for large clusters. The stability of clusters is analyzed by comparing the Gibbs free energy to the elastic energy in the system and is discussed as a function of the cluster size, curvature of the starting place, and temperature.

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I. INTRODUCTION

Spin-crossover compounds [1,2] are inorganic molecular materials switchable between two states in thermodynamic competition: the low-spin (LS) state, with a minimum spin multiplicity, and the high-spin (HS) state with the maximum spin multiplicity. These two states have several different physical properties, such as magnetic, optical, dimensional, and vibrational properties, which facilitate their study by different experimental techniques. The difference in molecular sizes between the two states, with the HS-state volume 3%–5% larger than the LS-state volume [3], is the premise for the creation of intermolecular interactions of elastic type which trigger the transitions between the two macroscopic HS and LS phases. If these interactions are higher than a threshold, then the transition between the two states is accompanied by abrupt hysteresis of various types (i.e., thermal, pressure, or light induced). These properties form the basis of promising applications, such as memory devices, sensors, or actuators [4–6].

The hysteresis properties have required the use of the concept of cooperativity as a result of short-range and long-range interactions which favor the spreading of clusters of molecules in the same spin state, so-called like-spin domains. However, until a few years ago, only indirect proofs for the existence of domains, such as the experimental determination of minor hysteresis loops [7] or Raman spectroscopy results [8], were available. In addition, these data were obtained on powder samples. Recent optical microscopy experiments [9,10], anticipated by a first effort 15 years ago towards the visualization of a spin-crossover compound structure during the transition [11], have provided excellent proofs of cluster spreading in spin-crossover single crystals of different shapes, such as rectangular, hexagonal, monoclinic, or orthorhombic, etc. These experiments have revealed the fact that clusters mostly develop from corners or around defects and eventually spread throughout the whole sample via an avalanchelike process. Elastic models that described the evolution of clusters from corners or edges [12–14] were proposed almost simultaneously with the first experimental data [15], which afterwards accelerated the in-depth study of these new models for spin-crossover compounds.

Indeed, models used previously for the study of spin-crossover compounds are not appropriate for describing the formation and evolution of clusters. The widely applied mean-field models [16], able to correctly describe macroscopic phenomena, especially in the case of gradual spin conversions and in the presence of light irradiation [17,18], do not allow any cluster formation. Ising-like models [19,20] with short-range interactions may allow cluster formation, but they grow from anywhere, either from the bulk or from the edges, which does not correspond to experimental observations. The main drawback of Ising-like models lies in the fact that they do not include the difference of molecular sizes between the HS and LS molecules and therefore the elastic interactions are ignored. Thus there is no possibility of obtaining distortions inside the crystal [13]. A recently introduced anharmonic Ising-like Hamiltonian [21,22] taking into account the elastic nature of the interactions by coupling the electronic and structural degrees of freedom of interacting spin-crossover molecules leads to local distortions which allow the nucleation and growth of like-spin domains [21–23].

In the so-called ball and spring models, the interactions originate just from the different molecular sizes between the LS and HS states; therefore these models are appropriate for the study of macroscopic domain formation and clustering. However, it was shown that in an elastic model applied

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[*] Corresponding author: cristian.enachescu@uaic.ro

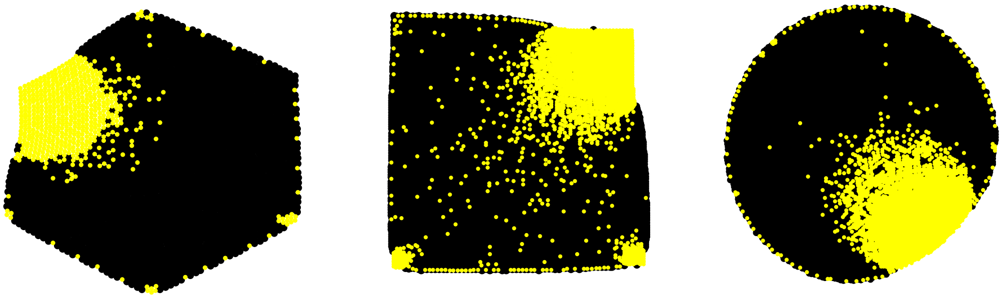

FIG. 1. (Color online) Clusters of LS molecules in a HS background spread from corners in hexagonal- and rectangular-shaped systems and from edges in a circular system.

with periodic boundary conditions the domain growth is hindered [24]. Therefore, the use of open boundary conditions is a necessary requirement for obtaining macroscopic clusters, at least in the harmonic case. Recent works showed that in an elastic model with open boundary conditions the nucleation always starts from corners (very rarely from noncorner edge sites), in either rectangular or triangular lattices. These results were obtained, either in the framework of molecular dynamics approaches [13] or using Monte Carlo Arrhenius [25] Metropolis dynamics [26], as well as by combining the molecular dynamics and Monte Carlo methods [27]. This general behavior was also supported by simple energetic considerations [27,28]. It has also been shown that in the framework of elastic models with molecular dynamics [13] the nucleation is a macroscopic process, with the size of the critical nucleus proportional to the total system size [29], and the importance of the shape effects has been underlined.

For circular systems, the absence of corners results in clusters starting from edges anywhere on the circular surface, both in the case of an elastic model with square symmetry solved by molecular dynamics treatment [29] or Monte Carlo simulations [30] and in the case of triangular symmetry studied by the Metropolis Monte Carlo method [26]. No preferential direction for cluster development in either lattice symmetry has been found.

Depending on the intermolecular interaction, modeled by way of a spring constant, one can observe one single cluster for strong interaction or several spreading clusters for weaker interactions. No cluster can be detected in the case of very weak spring constants, while impurities can slow down or even prevent the development of clusters [31]. The extremely high elastic energy determined by the (artificial) growth of a hypothetical cluster inside the bulk prevents this kind of cluster from spreading, at least as long as the lattice symmetry is maintained and cracking is not allowed. In Fig. 1, one can see examples of clustering from corners in the cases of hexagonal and rectangular systems and from edges in the case of circular systems, obtained for systems composed of around 40 000 molecules on a triangular lattice using Monte Carlo Arrhenius dynamics.

As stated above, the mechanoelastic model, which we use further on in this paper, was initially applied to hexagonal shapes, as it corresponds to the hexagonally shaped [Fe(bbtr)$_3$](ClO$_4$)$_2$ (bbtr = 1,4-di(1,2,3-triazol-1-yl)-butane) spin-crossover crystals [9,31–33] and later it was extended to circular isotropic shapes [26]. The theoretical two-dimensional (2D) approach is justified by the presence of typical experimental 2D spin-crossover solids, in which the metal ions are bridged by ligands in planes, defining a stack of layers, connected by weak interactions (van der Waals or hydrogen bond bridges). However, most spin-crossover compounds are not hexagonal, but crystallize in other shapes, either at the nanoscale or microscale or in the case of larger crystals. A very interesting situation is that of needle-shaped spin-crossover crystals which have been recently produced and used for potential applications for molecular actuators [34] or in ultrafast information processing [35]. Elongated crystals, also, provided textbook examples for the propagation of HS/LS interfaces, with quasi-1D behavior [27,36]. Therefore, it is important to study clustering in highly anisotropic shapes, such as ellipses, which are used also as sample shapes in other magnetic materials, such as nanopillars [37]. Moreover, the study of ellipses is useful as different points on their surface are characterized by different radii of curvature, with the smallest ones at vertices corresponding to the corners of hexagonal or rectangular systems and the largest ones at covertices, approaching infinity for elongated ellipses and then corresponding to linear edges. In addition, the control of the eccentricity of ellipses enables one to study systems with shapes changing from circular to needles.

The rest of this paper is organized as follows. First we present the model, and next we discuss the spreading of LS clusters in HS environments in ellipses of various aspect ratios. Then, two different kinds of dynamics, Eden-like and Kawasaki, are applied in order to determine the most probable cluster shapes. Finally, the stability of clusters is discussed in terms of their starting point, size, and temperature.

II. MODEL

In the 2D mechanoelastic model used in this paper, the molecules are located at the sites of a triangular lattice of elliptic shape with open boundary conditions. Every molecule, except those on the edge, has six nearest neighbors to which it is linked by connecting springs. In the fully LS or HS state, the system is in mechanical equilibrium, i.e., all the springs have their natural lengths. When a molecule flips, due to the different sizes of the two states, elastic forces are generated inside the system, starting from the nearest neighbors of the switched molecule. Consequently all molecules move, following an oscillatorily damped law, in order to find their new equilibrium positions (actually leading to minimization of the elastic energy of the spin-frozen system [26]). After every switch, all molecules change their positions, depending on their positions relative to the flipped molecule and to the edge of the system. Therefore the elastic spring constant generates both the short- and long-range interactions of the phenomenological Ising-like models used for spin-crossover compounds, as recently demonstrated analytically in the frame of an electroelastic model proposed by Slimani *et al.* [21]. Deformations appear inside the lattice and a position- and time-dependent elastic force, denoted here as the local pressure, acts on every molecule.

In order to establish which molecules switch, we need to define appropriate switching probabilities. The evolution of the system in the framework of the mechanoelastic model has been previously studied using either Monte Carlo Arrhenius-type dynamics based on the local pressure influence on every molecule or Monte Carlo Metropolis dynamics depending on the energy of the system. In the first situation, the transition probabilities from HS to LS and LS to HS can be written as [38]

$$P^{i}_{HS\to LS} = \frac{1}{\tau}\exp\left(\frac{D-k_BT\ln g}{2k_BT}\right)\exp\left(-\frac{E+\kappa p_i}{k_BT}\right), \tag{1a}$$

$$P^{i}_{LS\to HS} = \frac{1}{\tau}\exp\left(-\frac{D-k_BT\ln g}{2k_BT}\right)\exp\left(-\frac{E-\kappa p_i}{k_BT}\right), \tag{1b}$$

respectively. Here 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, $g = \exp(\Delta S/k_BT)$ is the vibronic HS-to-LS degeneracy ratio, while E corresponds to the activation energy of the HS $\to$ LS relaxation relative to a global reference state in which all the molecules are in the HS state. D is the energy difference between the two states in the case of noninteracting molecules, and p_i is the local pressure acting on molecule i, defined as $p_i = \sum_{\substack{\text{neighbors}\\ \text{springs}}} \frac{k}{A}\delta x_{ij}$ where k is the spring constant, A the molecular cross-sectional area, and $\sum_{\substack{\text{neighbors}\\ \text{springs}}} \delta x_{ij}$ the algebraic sum at mechanical equilibrium of elongations of neighboring springs (here taken positive for elongated springs and negative for compressed ones).

One can easily formulate the above probabilities in terms of energy. The Hamiltonian of the system (in the harmonic case) can be written as

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

where the first term corresponds to the classical Hamiltonian used to treat a spin-crossover Ising-type system (σ_i takes the value $+1$ for the HS and -1 for the LS state) and the second term stands for the elastic energy W_{elastic} calculated as the sum of energies for all the springs in the system.

Let us suppose that a molecule changes from HS to LS. Consequently, if its nearest spring elongations were δx_{ij} before the switch, then immediately after the switch (unrelaxed state) they become $\delta x_{ij} + \delta r$, where δr is the change in radius of the molecule. As the spring system has not yet relaxed to its new equilibrium configuration, this is a high-energy transient state of the system. The energy difference between the transient state and the initial HS state can be written as

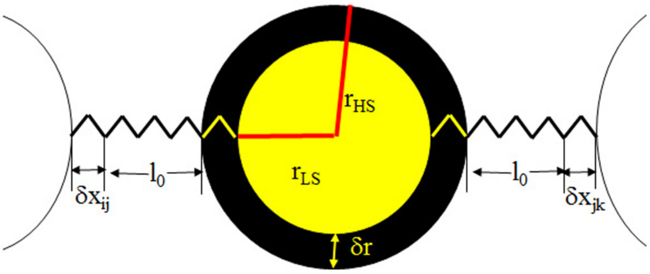

FIG. 2. (Color online) Variation of the elongation as a molecule flips from the HS to the LS state (l_0 is the natural length of the spring, r_{HS} and r_{LS} are the radii of HS and LS molecules, respectively, and δx_{ij} and δx_{jk} are the elongations before the flip).

$$\Delta W_i = -(D-k_BT\ln g) + \frac{k}{2}\sum_j\left[(\delta x_{ij}+\delta r)^2 - \delta x_{ij}^2\right], \tag{3}$$

where the sum is calculated over the nearest neighbors of the flipped molecule i. This means that the activation energy is simply the energy of all springs around a switched molecule compressed (or elongated) by the difference between the HS and LS radii (see Fig. 2). The relation (3) is transformed after a simple calculation as

$$\Delta W_i = -(D-k_BT\ln g) + \frac{k}{2}\sum_j (2\delta r\delta x_{ij} + \delta r^2). \tag{4}$$

In order to obtain the same probabilities as those in Eqs. (1a) and (1b), the equalities $E = \frac{k}{2}\sum_i \delta r^2 = \frac{kz}{2}\delta r^2$ (z is the coordination number, here 6 for bulk molecules) and $k = A\delta r$ must be respected.

During a Monte Carlo time step, each molecule of the system is randomly visited in order to decide whether it switches or not. For every molecule we compare the probabilities according to Eqs. (1a) and (1b) with a random number $\eta \in (0,1)$. A given molecule changes its state (and consequently its volume) only if this random number is smaller than the corresponding probability. After each successful switch, the new equilibrium positions of all molecules are calculated by solving a system of differential damped oscillatory equations, as discussed in previous papers [12,39].

III. RESULTS AND DISCUSSION

We have performed extensive simulations for elliptical systems on triangular lattices with Arrhenius dynamics in order to determine where clusters (domains) start from. In order to analyze the cluster stability as a function of temperature, all the simulations in this paper have been performed at a constant temperature below the transition temperature ($T = 100$ K if not stated otherwise), i.e., during a relaxation process. The parameters used in the model were $D = 1100$ K, $g = 1096$, $E = 400$ K, $\kappa = 2000$ K m^2/N, $k = 0.7$ N/m, $k_B = 1$, and $\delta r = 0.1 r_{HS}$. At first sight and by similarity with clusters

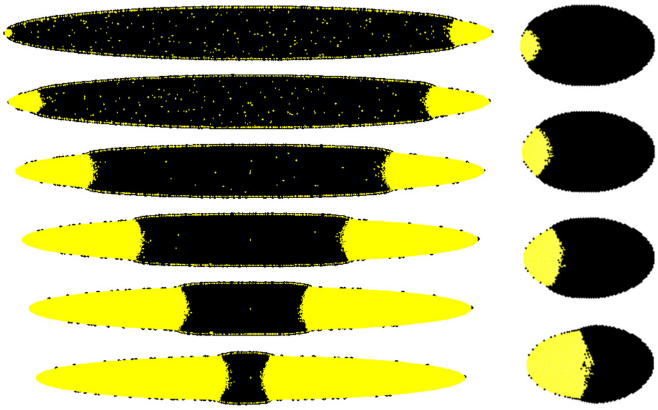

FIG. 3. (Color online) Left: Most probable cluster evolution at $T = 100$ K for highly elongated ellipses (high eccentricities; in this case the ellipses are composed of 46 969 molecules, with the ratio 10 between the major and minor axes of the ellipses and 720 molecules on the major axis). The two clusters join somewhere near the middle of the ellipse. Right: Possible spreading of one single cluster for smaller ellipses (in the figure the ellipses are composed of 4545 molecules, with the ratio 2 between axes and 100 molecules on the major axis).

growing from corners in the above-mentioned rectangular or hexagonal systems, one might expect that the nucleation would always start from the vertices of the ellipse, which are the points of maximum curvature. For most situations, this is actually the case, as represented in Fig. 3. In the initial state of the system, all molecules are in the HS state; then they are allowed to flip according to the probabilities (1a) and (1b). For large major axes, i.e., large distances between antipodal points of the ellipse, two clusters will spread starting from opposite vertices and join somewhere in the middle part of the ellipse (Fig. 3, left), with a similar kinetic and quasiconstant velocity as described in a previous paper and observed in experiments [27,28]. For smaller values of the major axis, the evolution of a cluster will in most cases prevent the spreading of another cluster from the opposite vertex (Fig. 3, right). The few switched LS molecules in the vicinity of the opposite vertex will be affected by the spreading of the first cluster formed and, under the effect of a lower local pressure, they will quickly switch back to the HS state. This nicely illustrates the long-range effect of the elastic interaction. For large ellipses, this effect will be attenuated and consequently there is a non-negligible probability of observing cluster spreading from both vertices. However, these general considerations have only a statistical value as it is possible that two opposite clusters form and then spread with comparable speeds even for small ellipses. Moreover, simulations carried out for ellipses with different eccentricities and at different temperatures have shown that these statements are valid only for ellipses with large ratios between major and minor axes (high eccentricities), while in the general case it is possible to obtain clusters starting from different sides of the ellipses, as one can see in the examples shown in Fig. 4.

In order to rationalize this complex behavior, we calculated the increase of the elastic energy associated with a cluster starting from different points of the edge. In previous papers [26,29] the total potential energy of the system was analyzed as a function of the relative size of a LS domain growing from the edge of a circular system, considering a contact (wetting) angle of $\pi/2$.

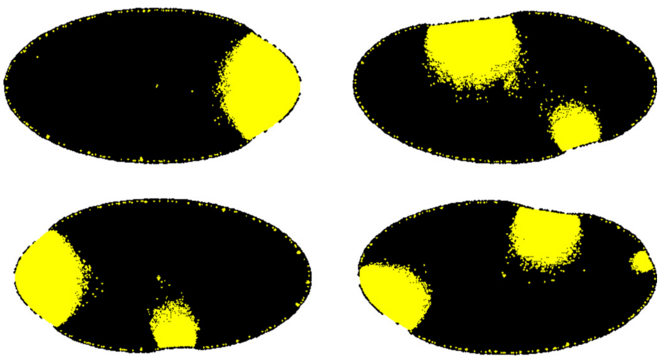

FIG. 4. (Color online) Examples of cluster evolution at $T = 100$ K for less elongated ellipses (lower eccentricities), resulting from independent simulations with various random seeds. The clusters occur not only at the vertices, but also at lateral points. The situation presented here corresponds to an ellipse composed of 46 443 molecules (major-to-minor axis ratio 2, 320 molecules on the major axis).

We follow here a more general approach which does not imply the *a priori* consideration of a wetting angle of $\pi/2$ [40]. Indeed, as recently discussed in Ref. [30], the wetting angle itself is the result of the lattice energy optimization including the deformation of the surface. However, a detailed study of the shape of the cluster (that is, the interface line between LS and HS domains) requires using advanced types of dynamics leading to better-defined borderlines, such as the Eden-like dynamics used below or the Kawasaki dynamics used in the following section.

The Eden-like dynamics used here is an extension of an approach developed by Eden for the growth of cell colonies [41]. Let us consider all molecules initially in the HS state, except for a LS cluster located in the vicinity of a selected point on the edge (typically around 50 molecules or 0.1% for an ellipse containing 50 000 molecules). In this way we created the seed (germ or nucleation site) needed for the subsequent spreading of the cluster. Following the genuine Eden method, the cluster is forced to grow by allowing the flipping of only HS molecules which have at least one LS neighbor (this means that only the HS molecules in the nearest vicinity of the cluster may switch). However, in the present extension of the method, once switched to LS, they are allowed to switch back. We randomly address all the molecules in the system and check if they have at least one LS neighbor. If so, we decide if the molecule switches or not by applying the probabilities (1a) and (1b) for HS and LS molecules. Earlier, it was pointed out that some differences can be obtained depending on whether one is addressing HS or LS molecules. The present method mimics surface tension by considering the total flipping probability of a HS molecule at the interface as proportional to the number of its LS neighbors (see [42]) and therefore should lead to a smoother interface than the alternative method. By this procedure we obtain a dynamical configuration of clusters. In contrast to the previous calculations presented in Figs. 3 and 4, only one cluster is allowed to grow, with a well-defined

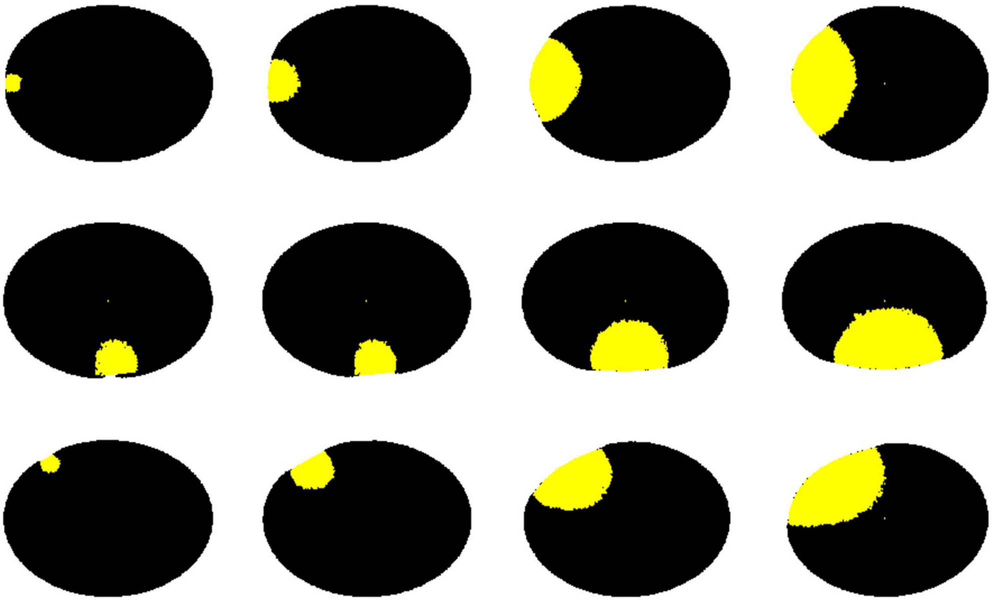

FIG. 5. (Color online) The growth of a cluster at $T = 100$ K from a vertex (top), a covertex (middle), or in between (bottom) obtained using an Eden-like dynamics as described in the text, for cluster size/ellipse area ratios of 1%, 5%, 15%, and 25%.

interface which is not blurred by the diffusion of LS states into the HS domain.

In Fig. 5 is presented the evolution of clusters starting from different points at the edge of the ellipse: at its vertex (peak), at its covertex (side), and in between these points. We notice that the cluster which starts from the in-between position spreads towards the vertex where the energetic conditions are more favorable and, from some point on, its evolution will be similar to a cluster starting from that vertex. On the other side, we notice also the fractal-like shape of the edge of the LS cluster, similar to that of the Eden model applied for cellular growth. As long as the clusters are not too large, their shape is close to circular; this feature seems to be more prevalent for the clusters starting from the covertex; consequently, the wetting (contact) angle varies. The study of the wetting angle on soft surfaces, defined as the angle from the horizontal of the ligand-vapor interface at the tip of the wetting ridge [43], is an actual problem for material scientists [44–46]. According to this definition, we can estimate the wetting angle using the tangential line at the initial surface (dashed green) and the HS/LS interface line (full red) from Fig. 6. With these considerations, the wetting angle θ seems to be somewhat bigger than $\pi/2$. However, an exact determination of the wetting angle is beyond the objectives of the present paper and would be difficult due to fluctuations at edges which result in large variations of this angle with time.

The Eden-like method provides clusters which grow dynamically and therefore do not necessarily correspond to a minimum-energy state. In order to minimize the energy, we therefore apply the Kawasaki dynamics [47,48], keeping constant the numbers of HS and LS molecules in the system. For this, we choose pairs of HS and LS neighboring molecules and exchange their states. In order to decide if the flipping of both molecules is accepted or not, we apply a standard Monte Carlo Metropolis procedure, by comparing the elastic energies in the system before the switch and after the switch when all the springs in the system have been relaxed. In this case, as the number of HS molecules is kept constant, the electronic energy does not play any role in the relaxation process; the probabilities (1a) and (1b) are not used here and the only role of the temperature is to determine how often a switch is accepted. The Kawasaki dynamics is more time consuming than the Eden-like dynamics; therefore the results presented here have been obtained for a smaller elliptic system, containing 4545 molecules, with major/minor axis ratio equal to 2.

In Fig. 7, we present the evolution of a cluster with an initially straight interface between the HS and LS domains. The application of the Kawasaki dynamics leads to a radial interface line perturbed only by thermal fluctuations. It is worth noticing that a similar final shape is obtained irrespective of the starting shape (i.e., a circular or linear interface) but important differences can be noticed in the case of different

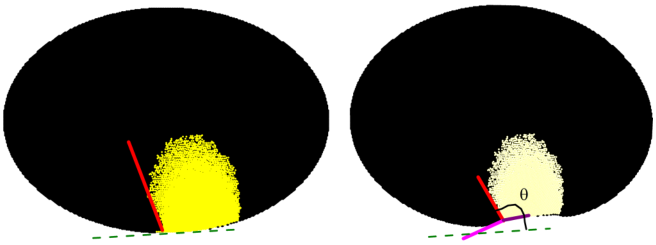

FIG. 6. (Color online) Determination of the wetting angle for a system with a 10% LS cluster starting from a covertex. Left: Hypothetical configuration of the system if the molecules were fixed. Right: Real configuration after the molecules have moved in order to minimize the elastic energy. The dashed green line is the original tangential line at the wetting ridge for a nondeformed system (fixed molecules). The solid red line follows the HS/LS interface line at the wetting ridge. The wetting angle is then the angle between the green and red lines.

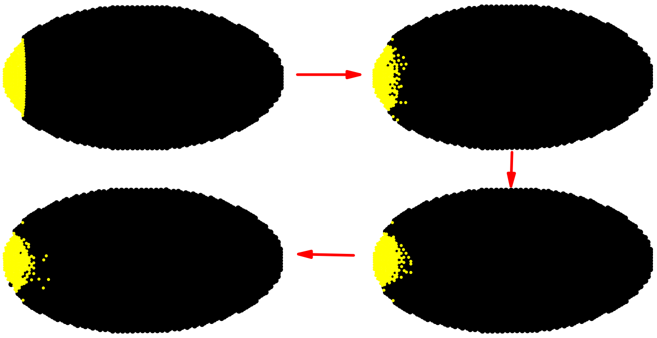

FIG. 7. (Color online) Evolution of the system using the Kawasaki dynamics for a cluster formed around a vertex with an area of 5% of the total ellipse area, with an initially linear interface between HS and LS states. $T = 0.005$ K; number of Monte Carlo steps (MCSs) 0, 1000, 10 000, and 100 000, respectively.

temperatures. There exists an optimal temperature for the fastest minimization of the system energy, in our case 0.005 K (see Fig. 8). In this case the interface is close to circular, which is reflected in the fact that its energy is very similar to the energy of the initial cluster with circular interface.

Obviously, this optimal temperature depends on the elastic constant and on the system shape. If the temperature is lower than the optimal one, then the thermal fluctuations are so small that the evolution of the system towards its lowest-energy state will be very slow (as in the case of 0.001 K) or almost absent for a large number of Monte Carlo steps (as in the case of 0.0001 K). If the temperature is somewhat higher than the optimal one, then the fluctuations will lead the system towards states with an elastic energy of the same order as that found by the Eden-like method (0.01 K). For a too high temperature, the too large thermal fluctuations will shift the system away from the minimum-energy state.

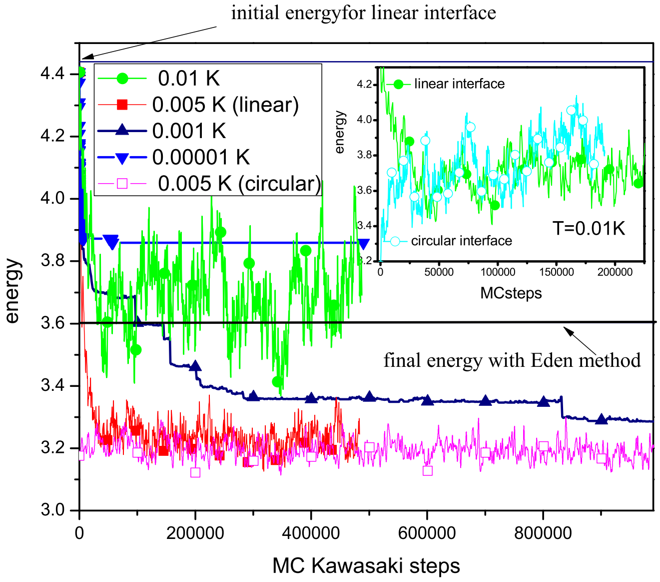

FIG. 8. (Color online) Energy evolution for a system with an initial cluster formed around a vertex, with linear (line with full symbols) or circular (line with open symbols) interface, in the framework of Kawasaki dynamics at different temperatures.

It is interesting to notice that regardless of the initial shape of the initial droplet, the final shape and energy depend only on temperature: in order to prove this we have compared the evolution of equivalent systems (the same LS fraction, 5%) with different initial shapes: with either circular or linear interface, or interface shape resulting from the Eden-like dynamics (Fig. 8, inset). In all three cases the final shape is similar, with a circular interface, and the energy fluctuates around the same value.

The situation is somewhat different in the case of the Kawasaki dynamics applied for a cluster formed near a covertex, presented in Fig. 9, for different percentages of LS molecules and considering the optimal temperature previously found for a cluster formed at the vertex (0.005 K). We notice that in this case the final energy is much smaller than the elastic energy for the circular interface (Fig. 9, bottom right); the final interface is still not too far from a circular one (as suggested by the white line in Fig. 9), but the local shape just near the edge is characterized by a wetting angle larger than $\pi/2$ (the red lines). If the LS fraction is lower than a critical value, then the initial cluster evaporates and the final state is a uniform "gas" of LS molecules in the HS background. This can already be observed in Fig. 9, where the LS cluster seems to be surrounded by a cloud of disconnected LS molecules. This behavior is similar to the Kawasaki dynamics applied on an Ising system [49].

In Fig. 10, we represent the total elastic energy of the spin-crossover systems as a function of the relative size of the LS domain and for different ratios of the major and minor axes of the ellipse. The results are obtained using Eden-like dynamics, as this corresponds to the cluster spreading and allows the study of larger systems, but similar conclusions can be drawn using the Kawasaki dynamics. In a previous paper [29], we studied circular systems with elastic interactions and showed that the cluster behavior is similar irrespective of the system size, with a critical nucleus proportional to the system size. However, in order to allow an immediate comparison between the behavior of ellipses with different eccentricities, we have chosen here ellipses having ratios of major to minor axes between 10 and 1 (the latter corresponds to a circle) but containing approximately the same number of molecules (between 43 853 and 47 839). For an accurate comparison, we study the elastic energy density instead of the total elastic energy of the system.

We notice that the elastic energy of the clusters approaches zero if a cluster starts from the vertex of a very elongated ellipse (actually, if the ellipse were to change into a line, this energy should be zero). These results are better interpreted as a function of the radius of curvature of the surface from where the clusters start (from infinity for the covertex of a very elongated ellipse to zero for the vertex of the same very elongated ellipse). Taking into account that for an ellipse with major axis $2a$ and minor axis $2b$, the radii of curvature at vertices and covertices are defined as $R = \frac{b^2}{a}$ and $R = \frac{a^2}{b}$, respectively, we represent in Fig. 11 the relaxed elastic energy as a function of the ratio between the radius of local curvature and the size of the cluster. Another useful representation is the dependence of the elastic energy on the length of the interface between the HS and LS phases: in the inset of Fig. 11 it is

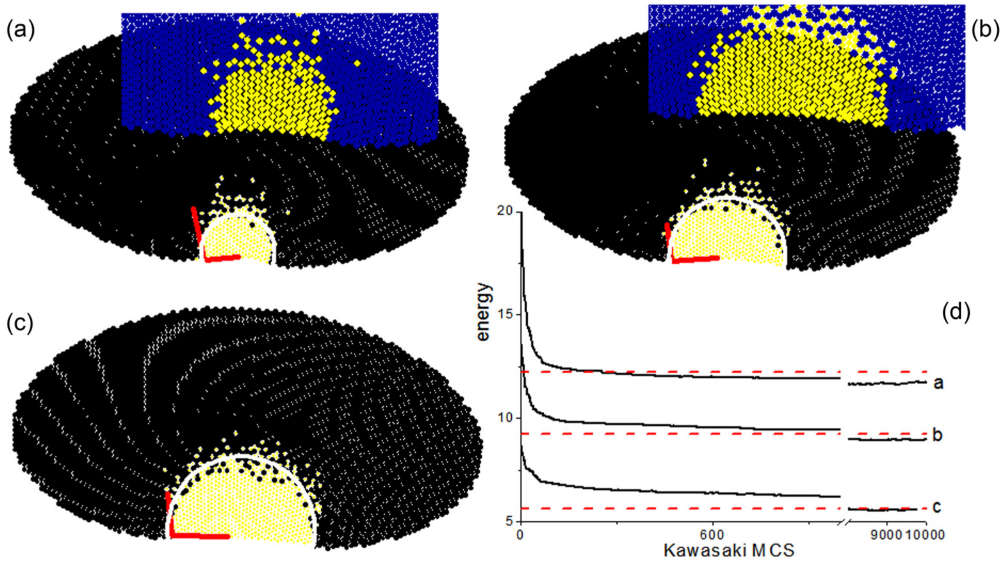

FIG. 9. (Color online) Final cluster shape in the Kawasaki dynamics at $T = 0.005$ K for systems with 5% (a), 10% (b), and 15% (c) LS fraction. In the zooms of (a) and (b) one can notice the deviation from circular shape of the interface just near the edge. (d) Elastic energy variation starting from a cluster with circular interface in the three situations (a)–(c) (full line) and comparison with the energy obtained using the Eden-like method (dashed red line).

shown that the longer the separation line, the higher the elastic energy. In other words, the minimum elastic energy of the system implies the minimum length of the interface.

In the following, we discuss the stability of a cluster as a function of its size, elastic energy, and temperature of the system. For this, we have chosen an ellipse with 47 389 molecules and a moderate ratio between the ellipses axis ($b/a = 132/99 = 4/3$). In Fig. 12, we represent the total elastic energy for the situations in which the cluster starts from a covertex, vertex, or intermediate point. Similarly to the results presented in Fig. 10, the elastic energy of the system is higher when clusters start from a covertex and lower if the cluster starts from a vertex. The total elastic energy when a cluster starts from some point between vertex and covertex approaches the energy of the vertex cluster while the cluster grows towards the vertex of the ellipse. This representation is useful for discussing the stability of a cluster as a function of temperature, as follows.

Taking into account the expression of the Hamiltonian (2), the variation of the Gibbs free energy of an N-molecule system when a number of N_{LS} molecules have switched from the HS state to the LS state can be written as

$$\Delta W_{\text{Gibbs}} = \frac{1}{2}\sum_i (D - k_B T \ln g)2N_{LS} = (D - k_B T \ln g) \times N\frac{N_{LS}}{N} = (D - k_B T \ln g)Nn_{LS}. \quad (5)$$

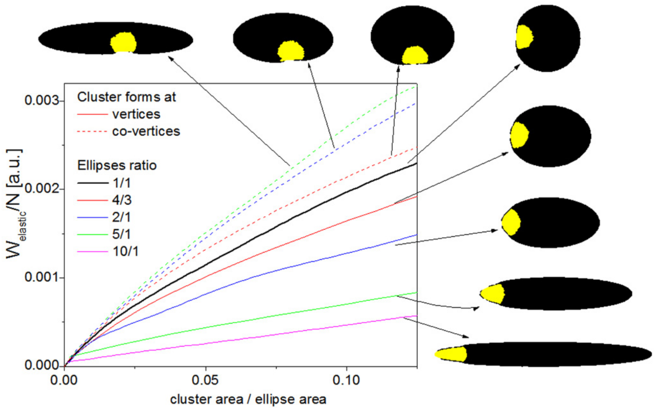

FIG. 10. (Color online) Normalized elastic energy increase as a function of the ratio between the cluster area and the total area (this ratio is similar to the LS fraction, that is, $1 - n_{HS}$ and usually denoted n_{LS}) for ellipses with different ratios between major and minor axes and for cluster seed at a vertex or covertex.

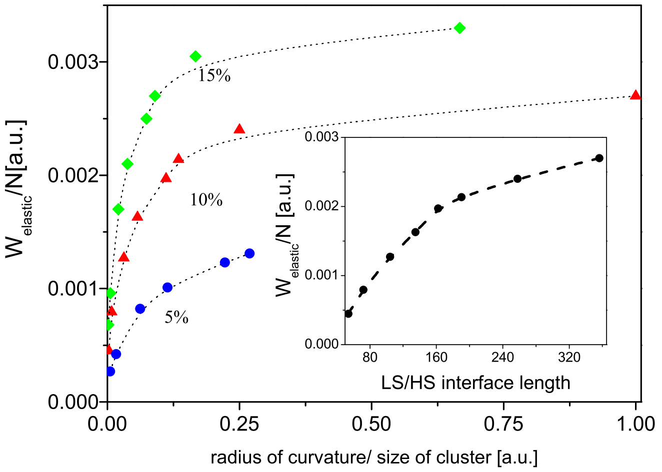

FIG. 11. (Color online) Normalized relaxed elastic energy for 5%, 10%, and 15% LS clusters as a function of the ratio between the radius of curvature at the starting point and the size of the cluster and (inset) as a function of the length of the HS/LS interface.

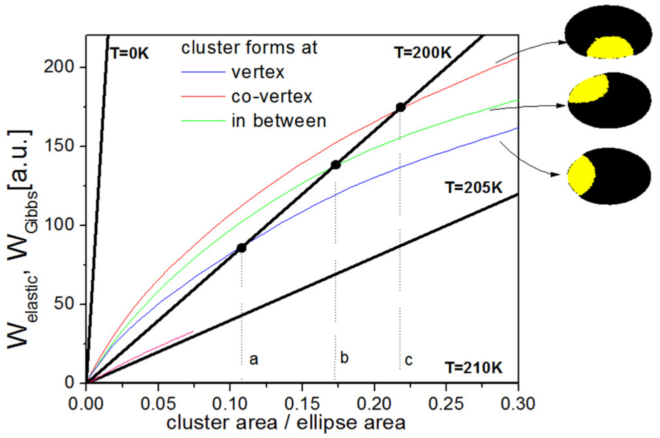

FIG. 12. (Color online) Stability of clusters resulting from the comparison between elastic energy and Gibbs free energy for nucleation points on different sides, as a function of temperature and cluster size.

ΔW_{Gibbs} shows a linear dependence on the ratio between the cluster size and the total size of the system. In the case of a temperature below the thermal equilibrium temperature ($T < \frac{D}{k_B \ln g} = 157.14$ K), where the LS state is the ground state, this line, which always passes through the origin of axes, has a positive slope. There might be an additional shape entropy term in ΔW, $-k_B T \ln(a/b)$, due to the fact that there is more space to form a cluster on a long side (near a covertex), but this might well be numerically negligible for the aspect ratios we can study.

This observation allows us to discuss the stability of a LS cluster as a function of its area and of the temperature of the system. If the gain ΔW_{Gibbs} in the Gibbs free energy is larger than the increase of the elastic energy $\Delta W_{\text{elastic}}$ of the system due to distortion, the cluster will be stable and may develop; otherwise it is unstable and will vanish.

In Fig. 12, we compare ΔW_{Gibbs} and $\Delta W_{\text{elastic}}$ computed as functions of the cluster relative area at various temperatures and for various cluster starting positions. Let us analyze the stability of a cluster starting from different sides of the ellipse as a function of the temperature. For $T = 200$ K, a LS cluster growing from the vertex will be stable if its relative area is bigger than the value $a \approx 11\%$ (see Fig. 12) of the total system size; while a cluster starting from a covortex will be stable if its area is larger than $c \approx 22\%$ of the total ellipse. If the cluster is bigger than the critical size, it will spread, while if it is smaller, it will shrink. It can be observed that a cluster starting from a vertex is stable for much smaller sizes; therefore the clusters develop from vertices with a higher probability. However, the threshold size decreases with decreasing temperature. From the diagram in Fig. 12, it can be noticed that if the temperature is smaller than a critical value, depending on intrinsic parameters of the systems, all LS clusters are stable, regardless of their size and starting positions. This critical value provides a thermodynamical definition of the HS → LS transition temperature.

IV. CONCLUSION

In this paper we have studied the shape and the stability of clusters of low-spin molecules formed in elliptically shaped spin-crossover crystals. Two methods have been introduced in order to study cluster formation and spreading: the dynamic Eden-like method and the Kawasaki dynamics which minimizes the cluster energy at a constant volume fraction. We have found that the stability of clusters depends not only on the place on the system boundary from which they start, but also on their size and temperature. The phase interface of clusters is close to circular for clusters starting close to the vertices of the ellipse, but presents some deviation from circular in the case of the covertex regions, with a wetting angle larger than $\pi/2$. Based on previous approaches for square systems on square lattices [13,21] and hexagonal systems on triangular lattices [25], a similar behavior is to be expected for high-spin clusters in a low-spin background during the LS-HS transition. However, in this case the interface between the HS and LS phases should be less well defined due to larger thermal fluctuations. Then, when the elastic constant is large (leading to wide hysteresis loops), a homogeneous region (mixture of LS and HS) is expected to appear, as we already noticed here in the case of LS clustering. The simulations realized in this paper can be useful for the design and/or the understanding of future experiments based on optical microscopy. Indeed, experimental studies of the shape and the orientation of the interface between the high-spin and low spin phases have recently been performed [27,28], with the aim of controlling the interface movement by fine-tuning of the relevant factors influencing the stability of the competing elastic domains, such as temperature. The experimental investigations are currently developing towards the control of local conditions, such as crystal shape or the curvature of the surface. In the future the clustering in realistic three-dimensional systems should be investigated, in order to predict the evolution of clusters in a large number of experimental spin-crossover systems.

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