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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

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Abstract

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 the 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. Contrary to the case of rectangular and hexagonal shapes, where the clusters always start from corners, we find that for ellipses clusters nucleate from vertices, co-vertices 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

The spin transition (ST) 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, 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, the 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 loops⁷ 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 fifteen 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 avalanche-like process. Elastic models that have described the evolution of clusters from corners or edges¹²⁻¹⁴ have been 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. Largely applied mean field models,¹⁶ able to correctly describe macroscopic phenomena, especially in the case of grad-

ual 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 formations, 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 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 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. Recent works showed that in the elastic model with open boundary conditions the nucleation always starts from corners (very rarely from non-corner edge sites), either in rectangular or triangular lattices. These results were obtained, either in the framework of Molecular Dynamics approaches¹³ or using Monte Carlo Arrhenius,²⁵ Metropolis dynamics,²⁶ as well as by combining Molecular Dynamics and Monte Carlo method.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 size²⁹ 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, either in the case of an elastic model with square symmetry solved by Molecular Dynamics treatment²⁹ or Monte Carlo simulations³⁰ as well in the case of triangular symmetry studied by Metropolis Monte Carlo.²⁶ No preferential direction for the 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 clusters spreading 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 case 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 $[\text{Fe}(\text{bbtr})_3](\text{ClO}_4)_2$ spin crossover crystals^{9,31-33} and later it was extended to circular isotropic shapes.²⁶ The theoretical two-dimensional 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 in between 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, 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 actuators³⁴ or in ultrafast information processing.³⁵ Elongated crystals, also, provided text-book example 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, 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/ rectangular systems and the largest ones at co-vertices, 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 starting point, size and temperature.

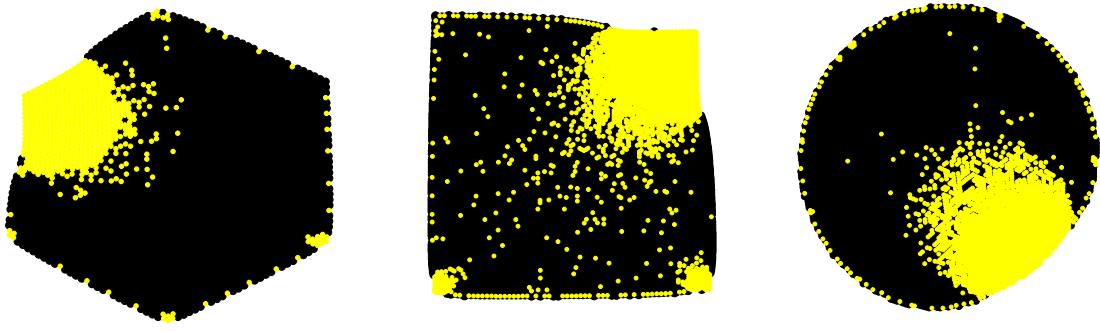


FIG. 1: (Color online) Clusters of LS molecules in a HS background spread from corners in hexagonal and rectangular shaped systems and from edge in a circular system.

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 states, 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 oscillatory damped law, in order to find their new equilibrium positions (actually leading to minimize the elastic energy of the spin-frozen system²⁶). After every switch, all molecules change their positions, depending on their relative positions 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 electro-elastic model proposed by A. Slimani et al.²¹ Deformations appear inside the lattice and a position and time dependent elastic force, denoted here 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 a Monte Carlo Arrhenius-type dynamics based on local pressure influence on every molecule or a 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

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

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

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, $g = \exp(\Delta S/k_B T)$ is the vibronic HS:LS degeneracy ratio, while E corresponds to the activation energy of the HS \rightarrow 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 non-interacting molecules, p_i is the local pressure acting on molecule i , defined as $p_i = \sum_{\text{springs}}^{\text{neighbours}} \frac{k}{A} \delta x_{ij}$ where k is the spring constant, A the molecular cross-sectional area and $\sum_{\text{springs}}^{\text{neighbours}} \delta x_{ij}$ 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:

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

where the first term corresponds to the classical Hamiltonian used to treat the spin-crossover Ising-type system (σ_i takes the value +1 for HS and -1 for LS) 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 radius change 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:

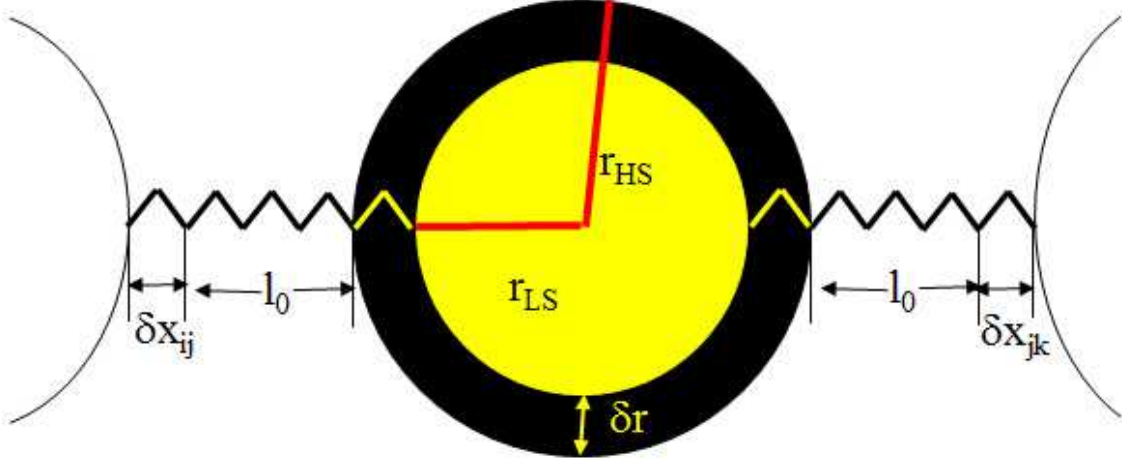


FIG. 2: (Color online) Variation of the elongation while a molecule flips from the HS to the LS state (l_0 is the natural length of the spring, r_{HS} and r_{LS} are the radii of HS and LS molecules, respectively, and δx_{ij} and δx_{jk} are the elongations before the flip).

$$\Delta W_i = -(D - k_B T \ln g) + \frac{k}{2} \sum_j ((\delta x_{ij} + \delta r)^2 - \delta x_{ij}^2) \quad (3)$$

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) with the difference between the HS and LS radii. The relation (3) is transformed after a simple calculation as:

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

In order to obtain the same probabilities as those in Eq 1(a,b), 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 equations 1a and b 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 ($T = 100\text{K}$ if not stated otherwise), i.e. during a relaxation process. The parameters used in the model were $D = 1100\text{K}$, $g = 1096$, $E = 400\text{K}$, $\kappa = 2000\text{K}\text{m}^2/\text{N}$, $k = 0.7\text{N}/\text{m}$, $k_B = 1$, $\delta r = 0.1r_{HS}$. At first sight and by similitude with clusters growing from corners in the above mentioned rectangular or hexagonal systems, one could 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 Figure 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,b. 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 quasi-constant 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 LS switched 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 to observe 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

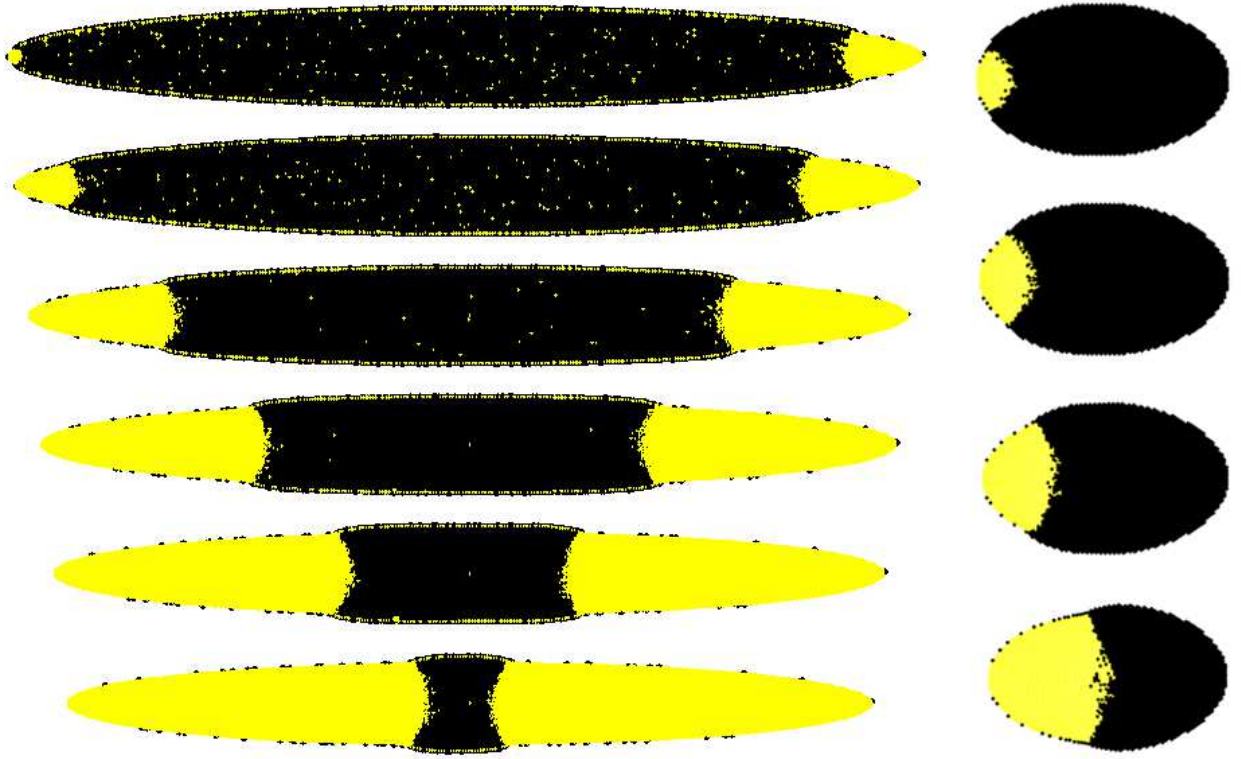


FIG. 3: (Color online) (left) Most probable cluster evolution at $T = 100K$ for highly elongated ellipses (high eccentricities; in this case the ellipses are composed of 46969 molecules, with a ratio 10 between the major and minor ellipses axes and 720 molecules on the major axis). The two clusters join 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).

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 $\pi/2$.

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.

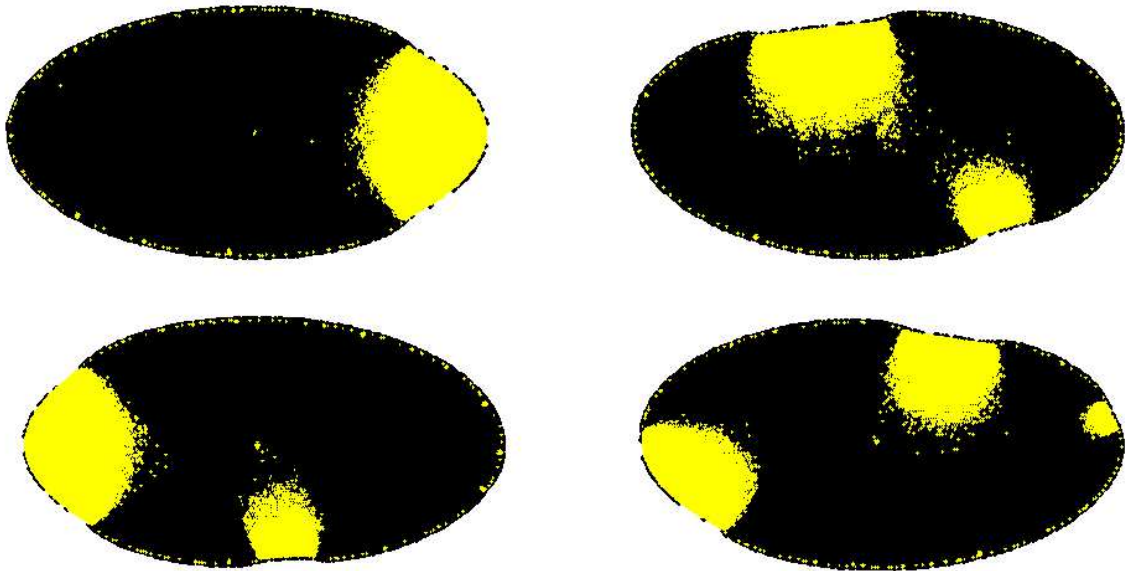


FIG. 4: (Color online) Examples of cluster evolution at $T = 100\text{K}$ for less elongated ellipses (lower eccentricities), resulting from independent simulations with various random seeds. The clusters occur not only at the vertices, but also at lateral points. The situation presented here corresponds to an ellipse composed of 46443 molecules (major/minor axis ratio 2, 320 molecules on the major axis).

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 fifty molecules or 0.1% for an ellipse containing fifty thousand 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 only allowing the flipping of the 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,b) 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

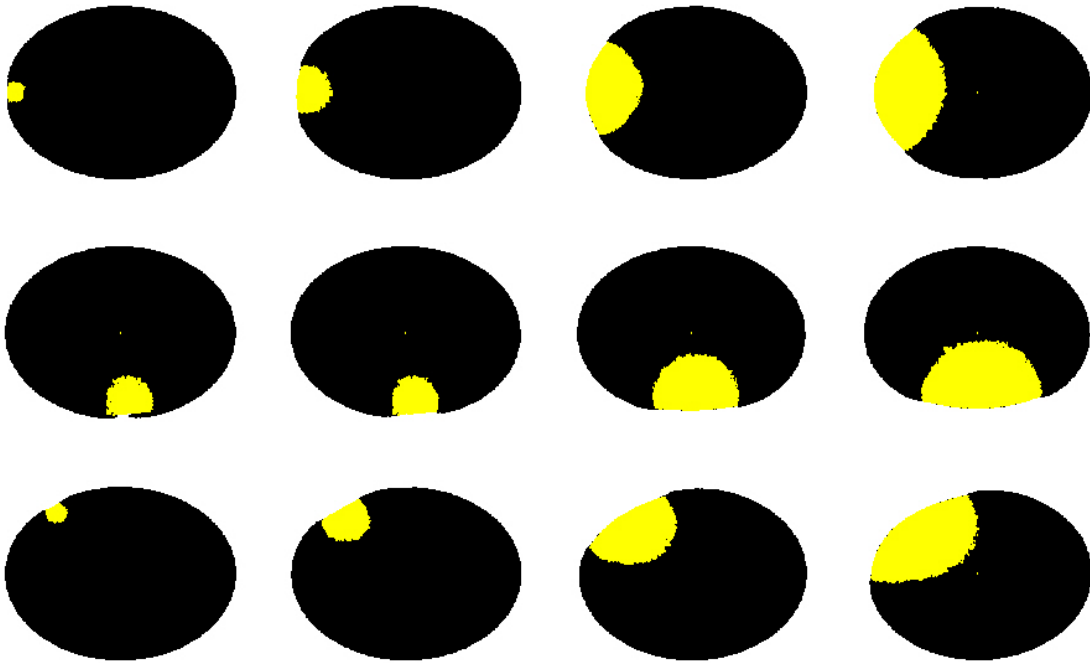


FIG. 5: (Color online) The growth of a cluster at $T = 100\text{K}$ from a vertex (top), a co-vertex (middle) or in-between (bottom) obtained using an Eden-like dynamics as described in text, for cluster size/ellipse area ratios of 1%, 5%, 15% and 25%.

to the number of its LS neighbors (see⁴²) and therefore should lead to a smoother interface than the alternative method. By this procedure we obtain a dynamical configuration of clusters. At variance from the previous calculations presented in Figs. 3 and 4, only one cluster is allowed to grow, with a well-defined 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 co-vertex (side) and in-between these points. We notice that the cluster which starts from in-between positions spreads towards the vertex where the energetic conditions are more favorable and, from a 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 circular; this feature seems to be more prevalent for the clusters starting from the co-vertex; consequently, the

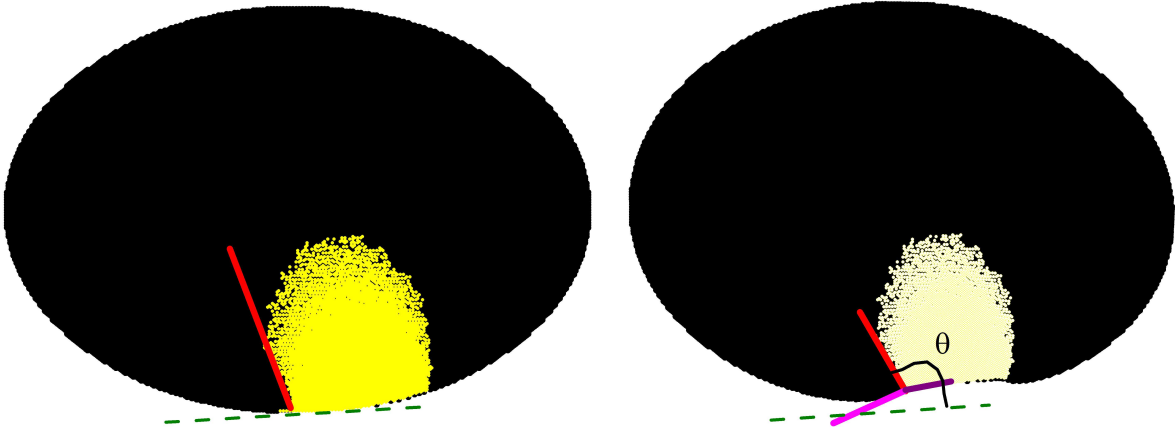


FIG. 6: (Color online) Determination of the wetting angle for a system with a 10% LS cluster starting from a co-vertex. (left) hypothetical configuration of the system if the molecules were fixed. (right) real configuration after the molecules have moved in order to minimize the elastic energy. The dashed green line is the original tangential line at the wetting ridge for a non-deformed 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 green and red lines.

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 finding of lower energy states; the probabilities 1a, b 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 figure 7, we present the evolution of a cluster with an initial 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. circular or linear interface) but important differences can be noticed in the case of different 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 by 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 (0.01K). For a too high temperature, the too large thermal fluctuations will shift the system away from the minimum energy state.

It is interesting to notice that regardless 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 (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 co-vertex, presented in Fig. 9, for different percentages of LS molecules and considering the optimal temperature previously found for a cluster formed at the vertex

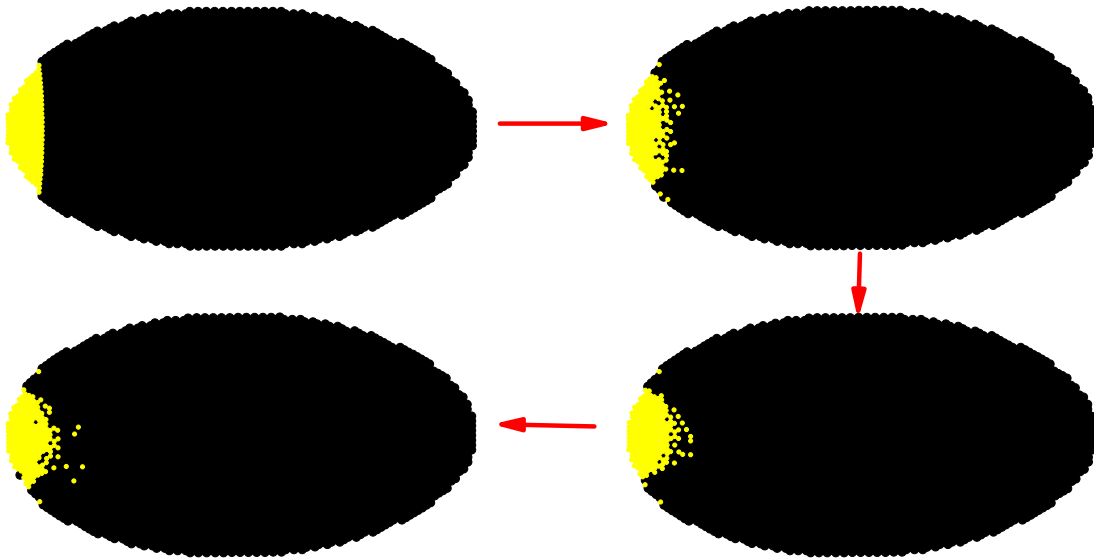


FIG. 7: (Color online) Evolution of the system using the Kawasaki dynamics for a cluster formed around a vertex with an area of 5% of the total ellipse area, with an initial linear interface between HS and LS states. $T = 0.005K$; MCS number: 0, 1000, 10000, 100000, respectively.

(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 $\pi/2$ (as 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 be already 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 the Eden-like dynamics, as this corresponds to the cluster spreading and allows the study of larger systems, but similar conclusions can be drawn by the Kawasaki dynamics. In a previous paper²⁹, we have studied circular systems with elastic interactions and we have shown 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

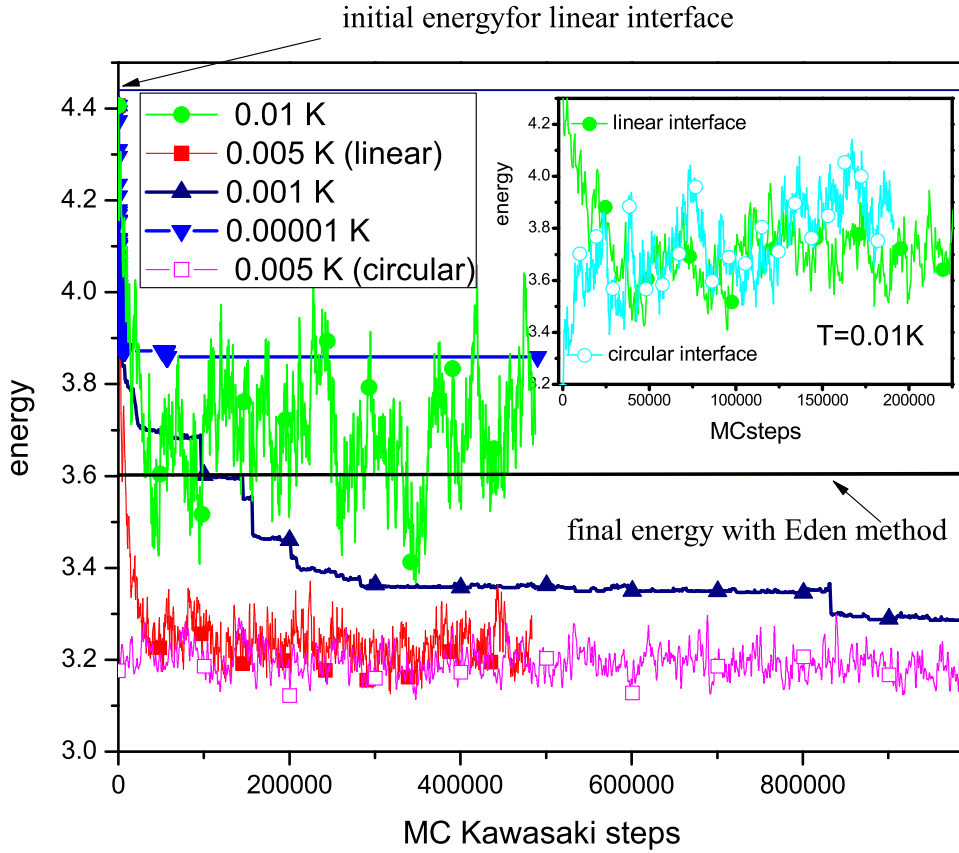


FIG. 8: (Color online) Energy evolution for a system with an initial cluster formed around a vertex, with linear (line +full symbols) or circular interface (line +open symbols), in the framework of Kawasaki dynamics at different temperatures.

eccentricities, we have chosen here ellipses having ratios of major/minor axes between 10 and 1 (the latter corresponds to a circle) but containing approximately the same number of molecules (between 43853 and 47839). 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 would 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 where the clusters start from (from infinity for the co-vertex 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

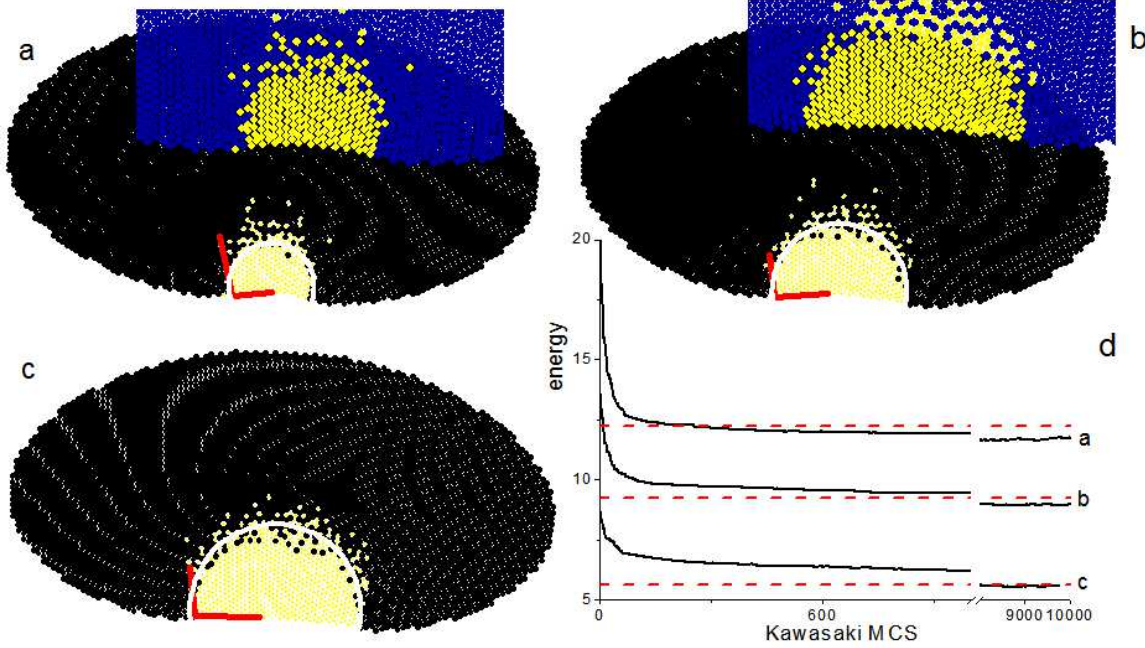


FIG. 9: (Color online) Final cluster shape in the Kawasaki dynamics at $T=0.005K$ for systems with 5% (a), 10% (b) and 15% LS fraction (c). In the zooms of (a) and (b) one can notice the deviation from circular shape of the interface just near the edge. (d) Elastic energy variation starting from a cluster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

vertices and co-vertices 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 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 47389 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 co-vertex, vertex or intermediate point. Similar to the results presented in Fig. 10, the elastic energy of the system is higher when clusters start from a co-vertex and lower if the cluster starts from a

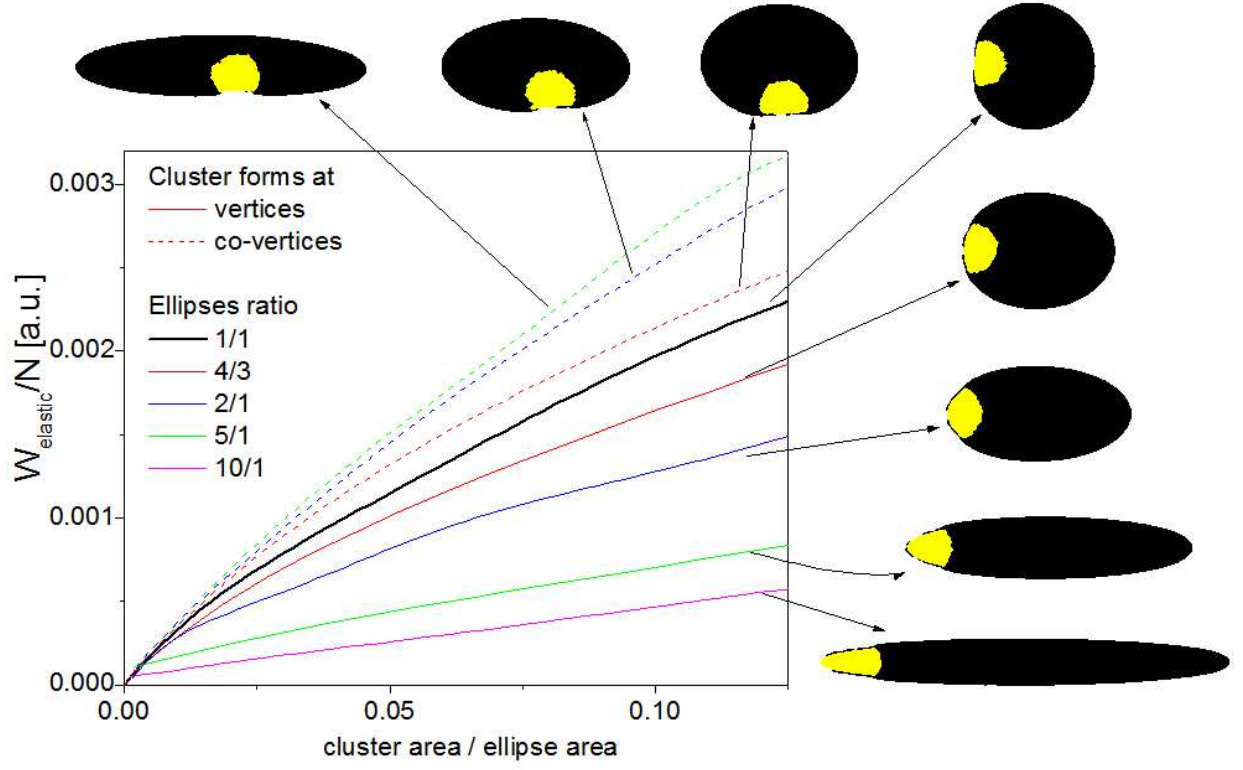


FIG. 10: (Color online) Normalized elastic energy increase as a function of the ratio between the cluster area and the total area (this ratio is similar to LS fraction, that is $1 - n_{HS}$ and usually denoted n_{LS}) for ellipses with different ratios between major and minor axes and for cluster seed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

vertex. The total elastic energy when a cluster starts from some point between vertex and co-vertex 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 a N -molecule system when a number of N_{LS} molecules have switched from the HS state to the LS state can be written as:

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

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

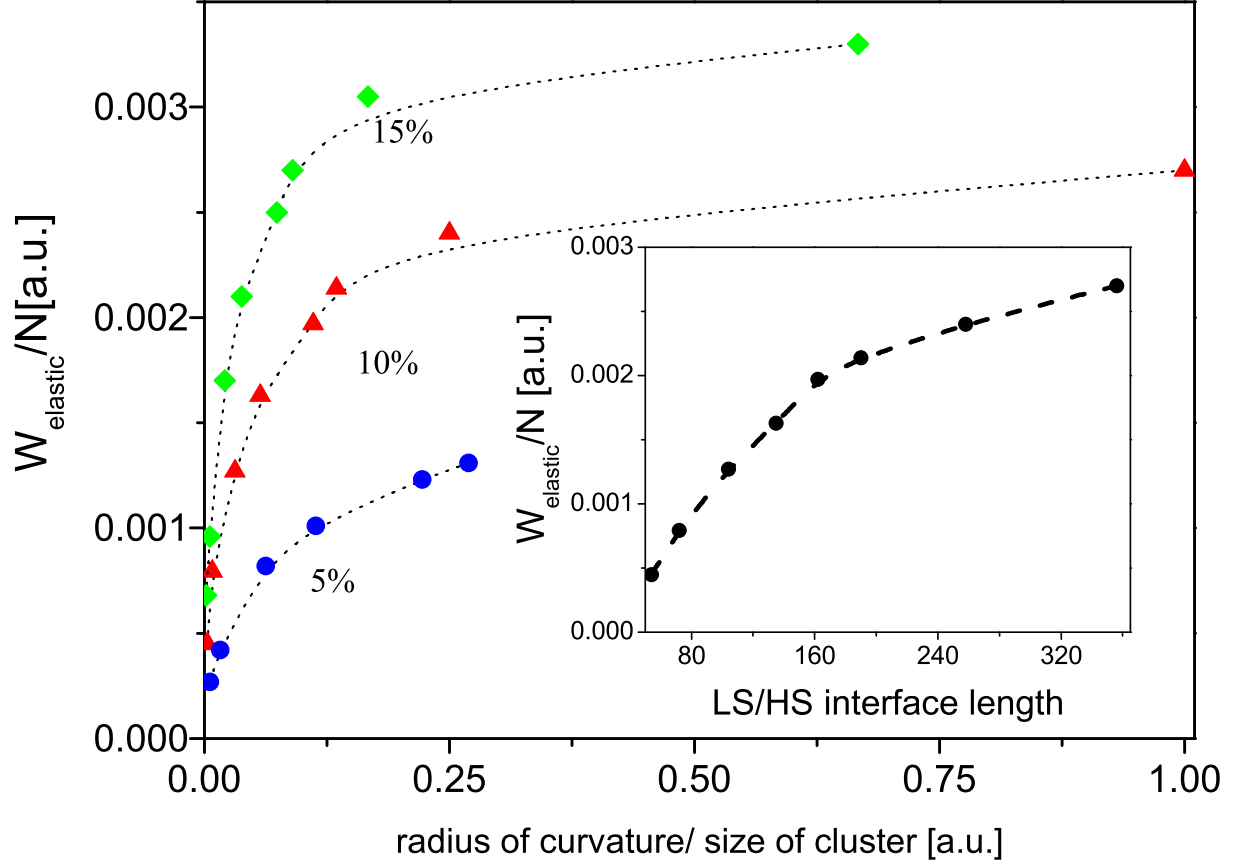


FIG. 11: (Color online) Normalized relaxed elastic energy for 5%, 10% and 15% LS clusters as a function of the ratio between radius of curvature at the starting point and the size of the cluster and (inset) as a function of the length of the HS-LS interface.

$\left(T < \frac{D}{k_B \ln g}\right)$, 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 co-vertex), 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 gain 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 $\Delta W_{elastic}$ computed as a function 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 $T = 200\text{K}$, a cluster growing from the vertex will be stable if its relative area is bigger than the value $a \approx 11\%$ (see figure 12) of the total system size; while a cluster starting from a co-vortex 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 \rightarrow 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 clusters energy at a constant volume fraction. We have found that the stability of clusters depends not only on the place on the system boundary they are starting from, 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 co-vertices 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 lattices²⁵ 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

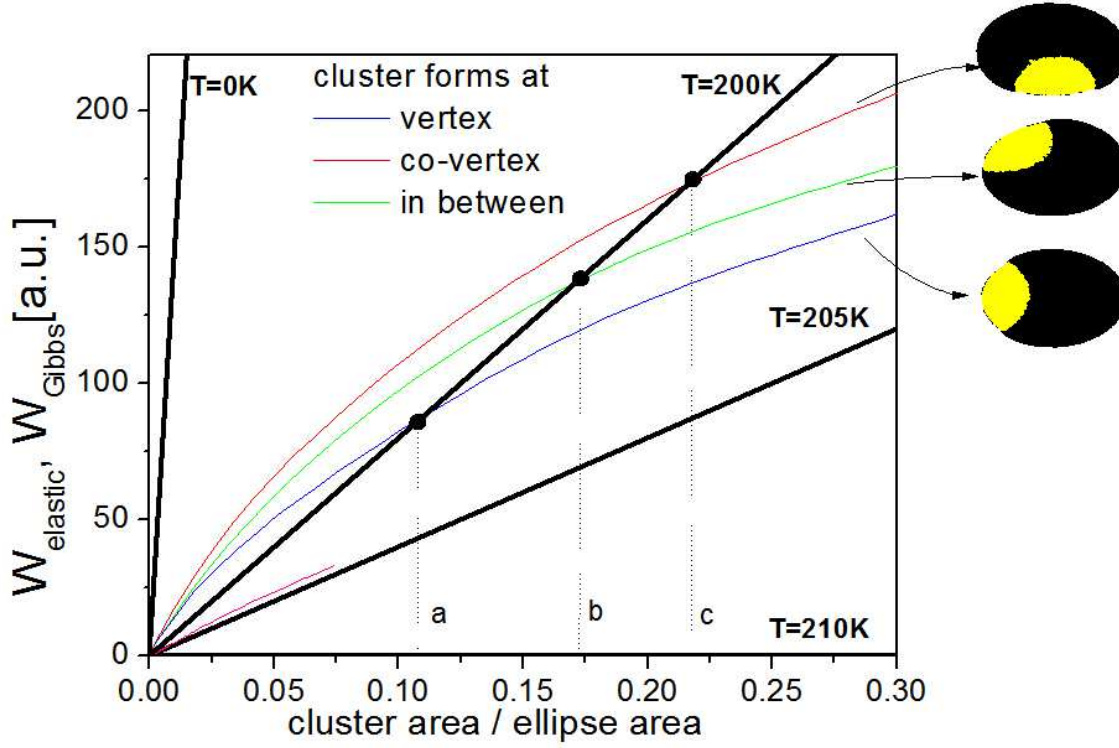


FIG. 12: (Color online) Stability of clusters resulting from the comparison between elastic energy and Gibbs free energy for nucleation points on different sides, as a function of temperature and cluster size.

here in the case of LS clustering. The simulations realized in this manuscript 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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