Growth of fractal electrodeposited aggregates under action of electric and magnetic fields using a modified diffusion-limited aggregation algorithm

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We have simulated the two-dimensional growth of fractal aggregates produced in electrodeposition experiments with axial symmetry in the presence of electric and magnetic fields. A modified diffusion-limited aggregation algorithm based on the Monte Carlo method is used in order to simulate cluster growth under the action of Coulomb and Lorentz forces, taking into account the thermal energy. The ion-particle movement has each step biased by the resultant force; in the algorithm, it is mediated by the Boltzmann term. The electric voltage between the electrodes tends to compact the aggregates and reduce the effect of screening. The Lorentz force provides a spiral form for aggregates which twists according to the magnetic field direction and intensity. A function was defined to measure the chirality of the system. The fractal dimension was also calculated to measure the influence of the electric and magnetic fields as well as the temperature during the growth process. Good agreement with experimental results was observed.

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I. INTRODUCTION

Patterns in nature have attracted the attention of mathematicians and physicists for a long time. Questions related to the growth of objects, like galaxies, bacteria colonies, or atom aggregates, are very intriguing and are in the realm of the modern physical activity.

In the beginning of the 1980s Witten and Sander proposed an algorithm to simulate the growth of fractal structures [1]. The model is based on interface growth through the irreversible aggregation of particles; such a process is limited by the particle diffusion. In light of the diffusion-limited aggregation (DLA) model a large number of fractal structures are well reproduced, even for structures of different natures [2,3].

Various examples of DLA-like aggregate growth occur in nature such as viscous fingering [4], bacteria colonies [5], and dielectric breakdown [6]. Under certain conditions the electrodeposition technique produces aggregates very similar to ones obtained through the DLA model [7–9]. Other forms such as dendritic, dense radial, and needle-like, among others, were also obtained by electrodeposition. Furthermore, these forms are dependent on the ion concentration and voltage between the electrodes. Beyond such usual electrodeposition parameters, external agents like pressure, temperature, humidity, and electromagnetic fields have been used to change the aggregate morphology [10–14].

This changing in morphology is particularly interesting when a magnetic field is applied. For a field applied perpendicular to the electrodeposition cell the fractal-like form of the aggregate becomes spiral [12,13]. A less intuitive picture was recently reported by Bodea *et al.* [14], who performed electrodeposition experiments with magnetic ions. For a magnetic field applied in the cell plane they observed a morphological symmetry breaking and the aggregate takes a rectangular shape.

In this paper we have developed a model based on the DLA algorithm in order to simulate in electrodeposition experiments the growth of structures with axial symmetry under a magnetic field perpendicular to the growth plane. We have introduced to the DLA algorithm a bias in the ion movement which is powered by the potential energy (or force) on the ion position. Thus, the electric and Lorentz forces are taken into account on the ion movement and the method can, at least in principle, be used considering any other forces. The dependence of the aggregate form on the electrical potential (V) between the electrodes or the magnetic field (B) is obtained. Two quantities are used to measure the change in the morphology: the fractal dimension and chirality. The theoretical results were compared with experimental ones.

II. MODEL

The original DLA algorithm proposed by Witten and Sander starts with a first particle (seed) placed in the origin of a lattice. A second particle located at some distance away moves in a random walk until it arrives at a site adjacent to the seed. The next particles are added at a random position away from the seed and move in a random walk until they encounter the cluster and aggregate and stick on its interface [1]. This process is repeated for N particles resulting in the aggregate. The particle movement is random; i.e., from a given position the particle has equal probabilities to go in up, down, left, and right directions. Further details of and many references to the DLA algorithm can be found in Ref. [3].

The major point in our work is how to take into account the forces acting on the ion movement to simulate aggregate growth in electrodeposition experiments. For the particle-cluster aggregation problem, which is in some sense similar to the electrodeposition, a model based on the Metropolis algorithm was proposed [15–17]. In these works a random point nearby the particle is chosen and the step to this new position is proportional to $e^{-K\Delta u}$, where K is proportional to the inverse of temperature and Δu is the variation of energy

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between the new and present positions. The net effect is to drive the particle movement towards the resultant force.

Mizuseki *et al.* [18] and recently Coey and collaborators [19,20] have reported interesting data on the growth of fractal aggregates by electrodeposition considering the effects of voltage, ion concentration, electrode shape, and magnetic field for circular and parallel electrode geometries. One of the most interesting results is the phase diagram as a function of ion concentration and electrode voltage, which exhibits nice and different possible aggregate forms (see Fig. 2 of Ref. [19]). The authors modeled the growth of aggregates by the use of the Laplacian equation, introducing further terms corresponding to the electric and magnetic fields [20]. According to their model, during the growth process an incoming particle feels the electric force only from the nearest particle in the aggregate. In our approach one takes into account the entire aggregate structure, and the manners of choosing the particle movement and, mainly, the magnetic field dependence are quite different and alternative from the model used in Refs. [18–20].

Our approach is based on the DLA algorithm, and we included the forces submitted to the particle, simulating what happens in electrodeposition experiments. In principle, the method can be applied to any other problem where a particle movement is biased by a force. Initially, a particle (seed of the aggregate) is placed at the origin of a square lattice. Another particle is launched some distance away, and it diffuses until it finds the cluster and finally it sticks to it. This procedure is repeated for all other subsequent particles. We consider that when the incoming particle sticks to the aggregate it changes its charge signal to the same charge of the aggregate and the particle remains in its position for all growth processes, as happens in real electrodeposition experiments. Furthermore, we assume that there is no charge redistribution during the growth. Such a conjecture can be considered true since good accordance between simulations and experiments is observed (see Sec. III A), even for metallic aggregates. For all the aggregates shown herein we stopped the growth for 10^5 particles. This size is limited by the time, computation which is enlarged by the long-range character of the Coulomb interaction, and as we shall see below, all particles in the aggregate are considered on a Coulomb interaction.

The potential or force is introduced in the choice of the direction of the particle movement. For each step, instead of having equal probabilities for the four possible choices, the particle follows a given direction according to the probability $e^{-K\Delta u}$ (see Fig. 1). K is equal to $1/k_BT$, and Δu is the variation of energy between the next and present positions. The Δu includes the Coulomb potential energy and Lorentz term. In the model k_B is stated as being 1.

We first introduce the Coulomb term. The electric potential energy between the incoming particle (q) and a particle (q_i) of the aggregate is given by $U_i=-q\left(\frac{q_i}{r_i}\right)$. Summed over all q_i particles of the aggregate the total electric potential becomes $U=-q\Sigma_{i=1}^{N}\frac{q_i}{r_i}$, where N is the total number of particles in the aggregate. Since all q_i are equal to q, U is then $-qq\Sigma\frac{1}{r_i}$. The summation $\Sigma\frac{1}{r_i}$ depends on the incoming particle coordinate (x,y) and on the aggregate form. If the incoming particle is too far from the aggregate, one can approximate r_i as d, d being the mean distance between the particle and aggregate. Therefore $\Sigma\frac{1}{r_i}=\Sigma\frac{1}{d}=N/d$. Thus $U=-q\frac{Nq}{d}=-q\frac{Q}{d}$. Q is the total charge of the aggregate. However, in the most interesting situations the incoming particle is close to the aggregate. The summation $\Sigma\frac{1}{r_i}$ is then equal to a number—say, n or $n(x,y)$. Thus, $U=-qqn(x,y)$. Rewriting this expression and inserting the total charge Q, one has $U=-qQn'(x,y)$, where $n'(x,y)$ is equal to $\frac{n(x,y)}{N}$ or $\frac{1}{N}\Sigma\frac{1}{r_i}$.

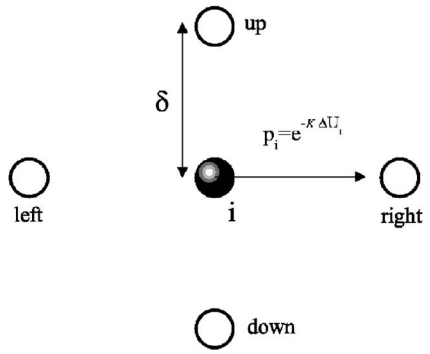

FIG. 1. Sketch of a step of the particle movement. See text for details.

The dependence on the voltage between the two electrodes can be inserted taking $Q=CV$, where C is the capacitance between the electrodes. In the model the two electrodes are considered too far away from each other, meaning that the electric field between the electrodes is well known. Nontrivial electric field structure, however, as will be discussed later (see Fig. 4), is observed only for distances close to the aggregate; going away, the field becomes radial (see the upper corner on the right of Fig. 4). Therefore C can be considered constant and independent of the aggregate size or form. Thus, the electric potential energy is given by $U=-qCVn'(x,y)$, with $n'(x,y)=\left(\frac{1}{N}\right)\Sigma_{i=1}^{N}\left(\frac{1}{r_i}\right)$.

The Lorentz term can be introduced using the form of the force between a charged particle and a magnetic field B_z applied perpendicular to plane of the movement of that particle: $F_l=-qvB_z$. The correspondent energy is thus $\left(\frac{\Delta u_l}{\Delta r}\right)_i=-F_{li}$, hence $\Delta u_{lx}=-v_yB_z\Delta x$ and $\Delta u_{ly}=-v_xB_z\Delta y$.

Another point we have to consider, also related to the Lorentz force, is the particle trajectory. Since the Lorentz force changes the direction of the movement, in a square lattice the particle tends to be restricted to move in square loops. Depending on the field intensity, mainly for high fields, the particles stay confined in small squares and do not move towards the aggregate. To avoid this behavior one averages the velocity over the last 10 steps. This averaging provides to the particle walk a trend of circular movement. The number of steps used in the average does not produce any effect on the form of the aggregate, at least between 5 and 20 steps.

In order to calculate the energy variation Δu used in the probability, one adds the Coulomb and Lorentz terms, and the energy variation in the x direction becomes, then, $\Delta u_x=-v_yB_z\delta_x+qCV[n'(x+\delta,y)-n'(x,y)]$. If the choice direction is in y, the energy variation is given by $\Delta u_y=-v_xB_z\delta_y+qCV[n'(x,y+\delta)-n'(x,y)]$.

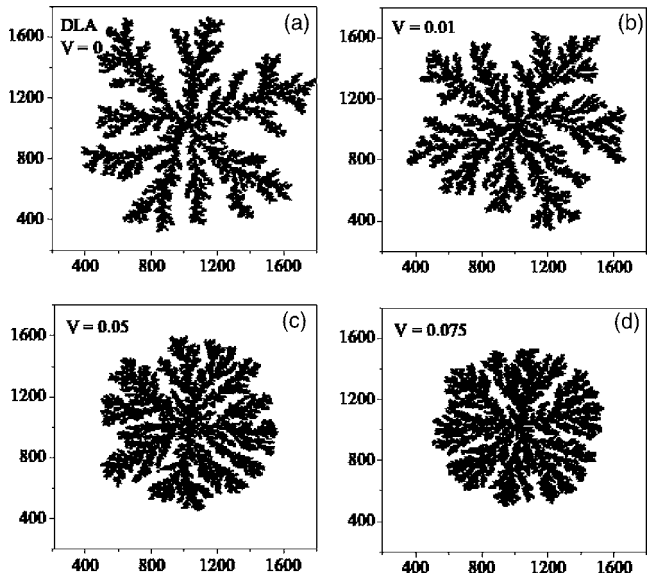

FIG. 2. Formed aggregates varying the electrical tension between the electrodes.

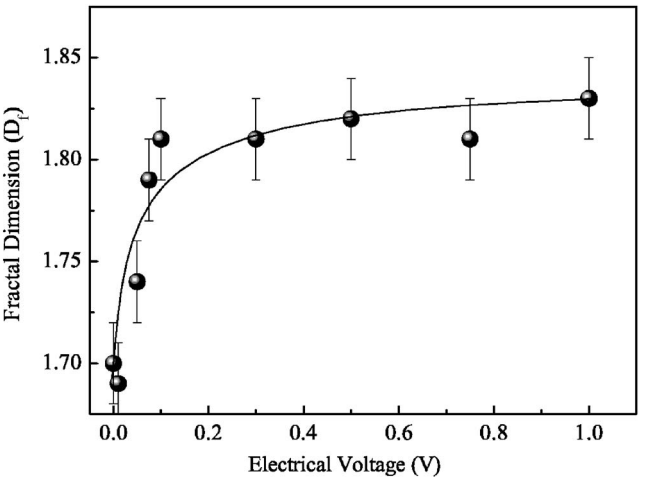

FIG. 3. Fractal dimension as a function of the electric potential between the electrodes. The line is a guide to the eyes.

In the original DLA model the particle chooses, in each step, a nearest neighbor between up, down, left, and right directions on its walking. In our model the particle can move to points distant from δ units (see Fig. 1). We have considered δ as being variable—i.e., different for each step. We considered δ as a random number or following a decreasing exponential distribution, but yet no change in the aggregate form was observed. For all data reported here we used an exponential distribution with mean value of δ equal to 2 without loss of generality.

The next step of the algorithm is a comparison between the probabilities relative to up, down, left, and right movements. It is performed by the Monte Carlo method with the use of a simple sampling. The probabilities p_i (i corresponds to one of the four possibilities and directions) are calculated and sorted in ascending order. A random number r between 0 and 1 is generated; if r is between p_i and p_{i+1}, the site $i+1$ is chosen. Notice that this procedure is different from the use of Metropolis [17]. Using Metropolis a random site i is chosen, and if $\Delta u_i < 0$, the movement is accepted and performed. If $\Delta u_i > 0$, the movement is accepted according to the probability $e^{-K\Delta u}$. A problem arises whether more than one or all Δu_i are negative. In this case the movement is equally accepted to any site i where Δu_i is negative, almost as a random walk, whereas according to our method the site $i$with the lowest energy is favored.

For relatively high values of V and B and therefore for Δu_i, the exponential $p_i = e^{-K\Delta u_i}$ attains too large or small values which can cause divergence or annul p_i, impeding a comparison between the probabilities. For this reason, in those cases one uses a normalization of the exponent of p_i by the energy of the central site i and p_i becomes $e^{-K\Delta u_i/(u_M - u_m)}$ (u_M and u_m are the maximum and minimum values between up, down, left and right sites). Such a procedure does not produce any significative change in the form of aggregates because it maintains proportion between the energies.

The only parameters of the model are V, B, and K, their units are volt, tesla, and J^{-1} (inverse of joule). The values used in the simulations do not correspond to the real values used in experiments. Only the relative intensities of V and B are relevant to the problem, which is focused on their influence on the form of the aggregates.

III. RESULTS AND DISCUSSION

A. Electric field dependence

Figure 2 exhibits the effect of growth under different voltages between the electrodes. Figure 2(a) shows the aggregate formed for the DLA growth; i.e., the particles are not submitted to any force in its random walk, except by the scattering by the medium. Applying a voltage the aggregate tends to be compact, the biasing produced by the Coulomb force provides a trajectory less random and more directed to the center [see Figs. 2(b)–2(d)]. It is worth noticing that the effect of screening that occurs on the small branches closest to the center is attenuated by the electrical potential.

To investigate the evolution of how compact the aggregates become with the application of an electric voltage we have calculated the fractal dimension. We used the counting box method.

For the DLA cluster the fractal dimension found is $D_f = 1.70 \pm 0.01$ [see Fig. 2(a)], in accordance with values reported in the literature (see, for instance, Ref. [3]). As exhibited in Fig. 3, increasing the voltage the fractal dimension increases and saturates around $D_f = 1.82$. In electrodeposition experiments performed by Matsushita *et al.* with Zn^+ ions an equivalent behavior was observed, and even the saturation value found in simulations agrees with the value observed in experiments [7]. However, for the experiment the fractal dimension increases only above a threshold value $V_c \cong 8$ V. Probably, there exists a minimum value for the electrical force intensity needed to overcome the random potential submitted to the Zn^+ ions on its diffuse movement.

An important detail in our algorithm is how the Coulomb interaction is taken into account in the model. We have considered the electric field from all particles of the cluster on the particle that moves towards some part of the cluster, in-

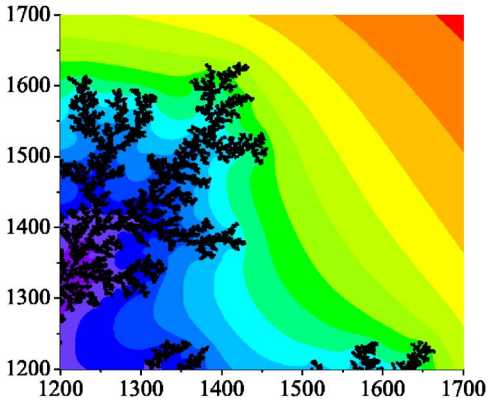

FIG. 4. (Color online) Electric field map in a region close to the cluster. It was calculated to the upper and right sides of the cluster shown in Fig. 2(b).

stead of considering only the central potential from the seed. The seed in the simulation corresponds to the central electrode in the electrodeposition experiment. Thus, when each particle sticks to the cluster it adds a tiny quantity to the total potential. Therefore, the trajectory of a given particle depends on the aggregate form; i.e., it depends on the past history of the particles already added to the aggregate. The long-range character of the Coulomb force should introduce a nonlocal effect on the growth process. Figure 4 shows a detail of the electric field map produced by the cluster shown in Fig. 2(b). This procedure changes the form of the equipotential surfaces from a circular or radial form to a more realistic one.

B. Magnetic field dependence

Figure 5 shows two aggregates grown in the presence of a magnetic field applied perpendicular to the plane in upward and downward directions. Beyond the bias towards the aggregate produced by the Coulomb force, the Lorentz force induces in the particle movement a bias in a circular direction providing to the aggregate a spiral form. The ensemble of particles behaves like a magnetofluid following a spiral movement. As is expected, changing the magnetic field direction, the aggregate spirals in opposite directions. The aggregates were grown under $V=0.01$ V, $K=0.01$ J^{-1}, and $B=\pm 10^{-4}$ T; without a field, they should correspond to the one of Fig. 2(b). Notice that the aggregates become more compact in accordance with the experiments performed by Mogi *et al.*; see, for instance, Fig. 2 of Ref. [13].

One interesting aspect related to the aggregate form is how to quantify the degree of twist produced by the magnetic field. To attack this question let us appeal to concepts related to the chirality of an object. An object is chiral if it is not coincident with its mirror image. The knowledge of whether an object is chiral or achiral can be useful, for instance, to determine the selection rules in optical activity, and important molecules responsible for the lifelike the DNA are chiral and appear only in one enantiomer. The chirality is a quantity that is expressed only by two values: an object is chiral or achiral. However, Le Guennec has recently shown

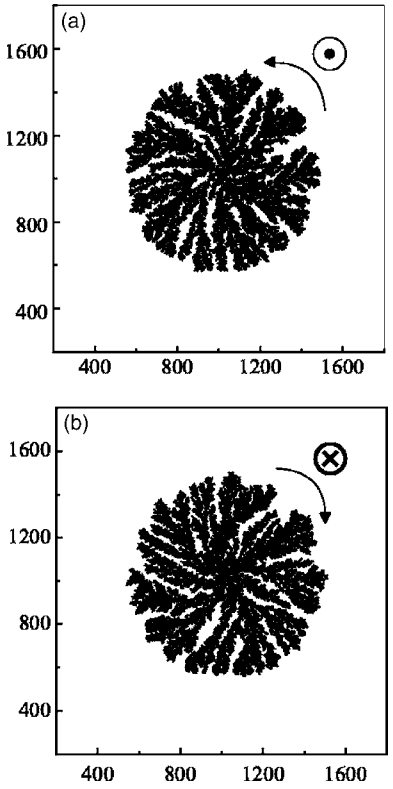

FIG. 5. Aggregates grown with a magnetic field applied perpendicular to the growth plane in (a) upward and (b) downward directions. B is $\pm 10^{-4}$; $V=0.01$ V and $K=0.01$ J^{-1}.

that in two dimensions chirality can be expressed by a continuous function [21]; i.e., chirality can assume continuous values between achiral and chiral forms. Inspired by the measure of chirality and by the work of Potts *et al.* [22], we propose an expression to quantify how spiraled the aggregate is. Such expression is given by

$$\chi = \frac{1}{N^2} \sum_j \sum_k \frac{\hat{r}_{1j} \times \hat{r}_{jk}}{|r_{jk}|}, \tag{1}$$

where j and k are the particle index and N is the number of particles in the aggregate. The first summation starts from the central particle spaning over j particles, and the second takes k-particle neighbors to a certain j particle. Actually, the second summation is restricted to a certain distance from j.

Taking only three particles, χ is zero if they are aligned and is maximum if they form a right triangle. For a cluster, due to the cross product, χ is zero if k particles are uniformly distributed around a certain j particle and attains maximum values if the k particles are preferentially distributed in a direction perpendicularly oriented to $\hat{r}_{1j}$. Hence, the spiral form of the aggregate is naturally quantified. A last point to consider is related to the range of the summation. Taking an arbitrary point in the aggregate, around it other particles are aligned in the twisted form and it tends to disappear for larger distances mainly for particles located in the opposite side of the cluster. Therefore, in order to take into account the local symmetry one takes in the summation only over k

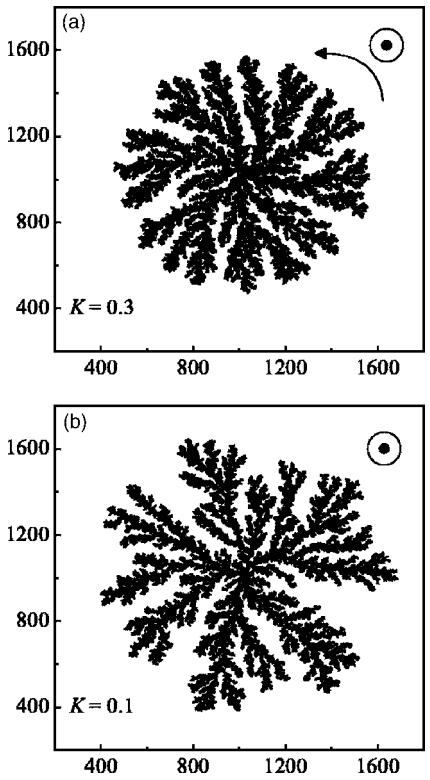

FIG. 6. Aggregates grown under a magnetic field ($B = \pm 10^{-4}$ T) at two different temperatures: $K=0.3$ J^{-1} and (a) and $K=0.1$ J^{-1} (b). $V=0.01$ V.

particles in the range between 40 and 100 distance units. The dependence on $1/|r_{jk}|$ is used to attenuate the effect of the cutoff range.

Using Eq. (1) we calculated the function χ for the aggregates shown in Figs. 5 and 2(b), which correspond to aggregates grown under opposite fields and without a field, respectively. For them, we found χ equal to 1.44×10^{-6} [Fig. 5(a)], -1.71×10^{-6} [Fig. 5(b)], and 1.61×10^{-7} [Fig. 2(b)]. To obtain these values we used a cutoff range of 40 units; for other values up to 100, it is almost the same. The values found are approximately symmetric for opposite fields and 10 times smaller when the aggregate is grown without a field. The fact that χ does not vanish for a growth without a field is related to the intrinsic nature of χ, which measures the chirality, and since the aggregate of Fig. 2(b) is achiral, χ is not null. Actually, structures with spiral form are yet more achiral with larger χ values.

C. Temperature dependence

Another interesting aspect of the aggregate growth is the lost of symmetry that occurs with the temperature changing. Figures 5(a), 6(a), and 6(b) exhibit a sequence of aggregates grown under a magnetic field at increasing temperatures $K=1$, 0.3, and 0.1 J^{-1} ($K=1/k_BT$), respectively.

Comparing the structures grown at $K=1$ and 0.3 J^{-1} one observes that the clusters are less compact and the spiral form is lost at $K=0.1$ J^{-1}, transforming the cluster in a DLA-like structure. The continuous variation from spiral to DLA

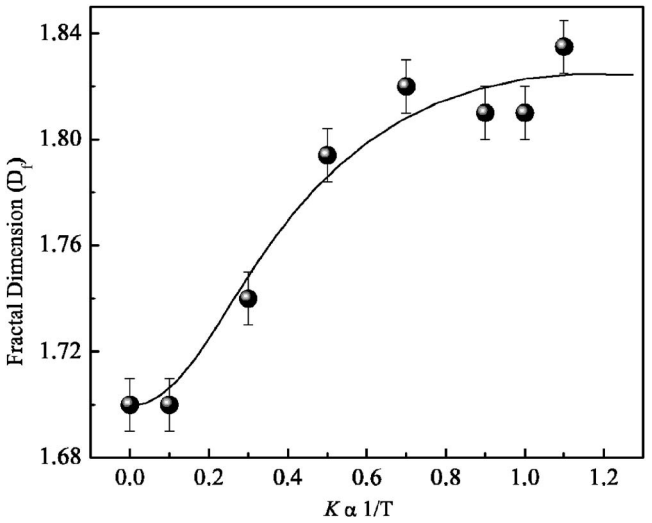

FIG. 7. Fractal dimension calculated for different temperatures for aggregates grown under a magnetic field. $K=0$ corresponds to the DLA-like structure. The line is a guide to the eyes.

structure can be better analyzed from fractal dimension and chirality calculations.

Starting from $K=1$ J^{-1} and decreasing K—i.e., increasing the temperature—the fractal dimension decreases and tends to the fractal dimension of the DLA structure (see Fig. 7). $K=0$ corresponds to the limit of infinite temperature; there is no bias direction in the particle movement. Such a variation of the fractal dimension is the changing in the compactness of the aggregate structure. The error bars come from the counting box method calculation.

For the chirality this continuous variation is also observed, it illustrating the loss of spiral structure (see Fig. 8). It illustrates that the limit of large temperatures even with applied field tends to the DLA structure, as should be expected due to the disorder induced by the temperature. The

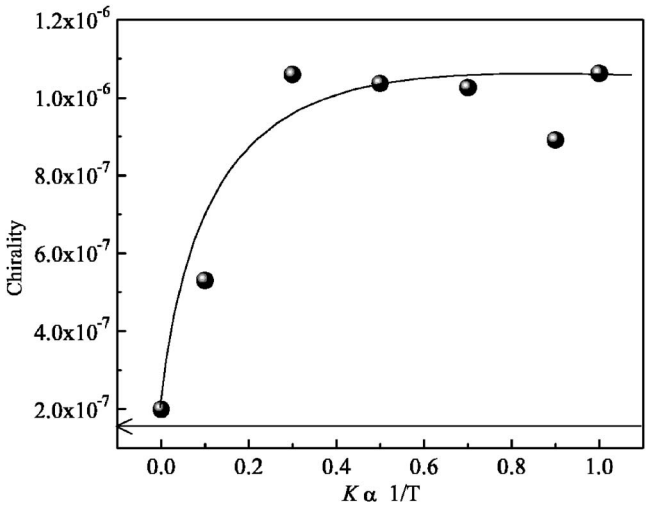

FIG. 8. Chirality calculated for different temperatures for aggregates grown under a magnetic field. The base line (arrow) corresponds to the chirality for an aggregate grown without a field. The line is a guide to the eyes.

arrow in the graphics is a base line that corresponds to the chirality of an aggregate grown without a field. It is interesting to notice that although the chirality decreases continuously and vanishes for a certain K value, it does not mean that a phase transition occurs in the strict thermodynamical sense. K does not vary continuously, each point in the graphics corresponding to a different growth event.

The chirality calculation is very sensitive to the details of the short-range scale on the aggregate structure; thus growing structures repeated times with the same parameter provide some dispersion on the χ value. Since the growth of such structures is relatively very time consuming, we did not obtain the error bars.

The main effect of the thermal energy is to increase the degree randomness of the particle movement, which provides a loss of bias in the circular direction induced by the Lorentz force.

D. Final remarks

The influence of electric and magnetic fields and the temperature on the growth of electrodeposited aggregates described above can be considered perturbations to the standard DLA model. They are agents that provide a bias on the random particle movement. The fractal character of the simulated aggregates is not destroyed, and indeed they reproduce the forms obtained in electrodeposition experiments. This accordance is obtained in spite of the simplicity of the model; notice that we did not consider realistic physicochemical mechanisms of electrodeposition processes.

IV. CONCLUSION

In this paper we have simulated the two-dimensional growth of structures in electrodeposition experiments under the action of electric and magnetic forces and the thermal energy. Based on the standard DLA model we introduced different probabilities on the random walk step. The probabilities are weighted by the Boltzmann term, and the step direction is chosen by the Monte Carlo method. It provides a bias on the particle movement until the particle sticks in the aggregate.

The effect of the electric field on the growth is to compact the aggregates, increasing the fractal dimension from 1.70 to 1.82. This evolution saturates after the application of a few volts. The effect of screening is attenuated, and inner branches also grow due to the bias to the center on the particle movement. We considered the entire aggregate contributing to the electric field acting on a traveling particle. Besides introducing a dependence on the history of growth, it modifies the aggregate form. The magnetic field tends to produce a spiral form on the aggregates, and they twist to opposite directions according to the field direction. A quantity, stated as the chirality, was defined to measure how twisted the aggregates are.

Increasing the temperature the thermal energy introduces noise to the particle walk, diminishing or vanishing the bias introduced by the forces. For structures grown under electric and magnetic fields the introduction of noise due to thermal activation of the structures is accompanied by a decrease of the fractal dimension and chirality. The structures obtained in our simulations are in good agreement with experimental results.

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