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A New Model for Crystal Growth under High Magnetic Field -Effect of Environment in Diffusion-Limited Aggregation-*

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A new Monte Carlo model is introduced to describe the Diffusion-Limited Aggregation (DLA) with extra forces arising from the Lorentz's and/or Coulomb forces. Specific patterns grown under the external force are produced by Monte Carlo simulation. In the present model, the basic movement of particles is the random walk, with different transition probabilities in different directions, which characterize stochastically the effect of the extra forces. In some cases, pattern-formations which are qualitatively different from the standard DLA model are observed and they are compared with preexisting experiments.

KEYWORDS: fractal dimension, Diffusion-Limited Aggregation (DLA), magnetic field, crystal growth, computer simulation, random walk, Monte Carlo method

1. Introduction

Diffusion–Limited Aggregation (DLA) in 2–dimensional space is a well-known physical phenomenon having a beautiful branching pattern with fractal dimension of 1.67 [1]. Much attention has been paid to DLA model in the field of crystal growth and pattern formation, because this model exhibits fascinating statistical properties in spite of its simplicity.

However, the growth process is very complicated if it includes environment, such as electric field, gradient of temperature, convection in system, and so on. Sawada *et al.* explored a problem of dendritic growth in electrochemical deposition of zinc from zinc sulfate solution [2]. In the research, they discovered that the pattern and the growth rate depend on the ion concentration in solution and also on the applied voltage in the experiment. Similar experiments [3] [4] have also been reported by other groups. As a matter of fact, the standard DLA model does not explain the effect of these environments. To examine the pattern grown under external force, several kinds of perturbations have been included to extend DLA growth mechanism [5] - [8]. The effect of drift of ion in electric field was also investigated[6].

As a new type of perturbation, Mogi *et al.* at our Institute applied a high magnetic field for the dendritic growth of silver [9] [12] [13], lead [10] [12] and zinc [11] [12] in solutions and obtained new specific patterns of metal leaves. They suggested that the changes in growth patterns arise from magnetohydrodynamic effect on diffusive motion of metal ions.

In the silver case, they have used a chemical reaction such as

$$Cu + 2Ag^{+} \rightarrow Cu^{2+} + 2Ag \downarrow \qquad (1)$$

and applied a high magnetic field up to 8T. The obtained patterns are specifically different from the standard DLA. Under high magnetic field, the branches bend slightly and the shape of the emvelope becomes circular. This result implies that the particle diffusion in the medium is strongly affected by the magnetic field and this decisive difference in the particle movement changes the final pattern. Since the direction of bending is reversed, if the magnetic field is reversed, the observed bending of the dendrite is attributed to the cyclotron motion of the Ag ions. These experimental works have also shown that the effect of magnetic field is fundamentally universal, i.e., independent of the details of the chemical properties of the solution. Therefore, it is expected to be able to reproduce this universality observed in the experiments via computer simulation. Moreover, it would be an interesting subject if we could control the fractal dimension, which is thought to be a universal constant, using the high magnetic field. This would imply a possibility to develop a new material having desirable shapes. The primary aim of this paper is to examine various patterns of crystal growths under the external force involving the stochastic treatment of the cyclotron motion.

The present paper is organized as follows: A new growth model is introduced in the next section, which is an extension of the standard DLA model using a Monte Carlo method with external pertubations. A large computer simulation is performed and the obtained numerical results are given in Section **3**. They are also compared with the experimental observations. Sections **4** and **5** are devoted, respectively, to Discussion and Conclusion.

2. Model and Numerical Method

The present model is basically a Monte Carlo simulation on a square lattice. We assume three environments in crystal growth, which are shown in **2.1** high magnetic

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field, **2.2** gradient of ion concentration and **2.3** electric field.

2.1 Magnetic Field

First, special attention is made for the effect of applied high magnetic field. Here, the random walk of charged particles affected by magnetic field is described by changing stochastically the preference of the direction of motion perpendicular to the previous walk vector. By this simple technique to change the probability of movement, fundamental aspect of the migration under magnetic field is taken into account. Accordingly, this model incorporates both diffusion and cyclotron motions and mimics the process and produced morphologies that resemble the experimental condition [9]. This model is explained graphically in Fig. 1. Figure 1 (a) shows the equal probability of each four direction for movement in the standard DLA on square lattice. In this case, the growth pattern has open and randomly branched structures with no natural length unit, so that it is categorized into fractals. On the contrary, the ion under high magnetic field is affected by the Lorentz force. Figure 1 (b) introduces the present model including the probability of direction changed by environment. The direction of the movement is defined not stochastically but by the present position and the position at previous N steps. The next direction of movement is fixed by the Lorentz force parameter θ. For $\theta = 0$, the movement of particle is ballistic. For $\theta > 0$, the movement of particle is affected by the Lorentz force.

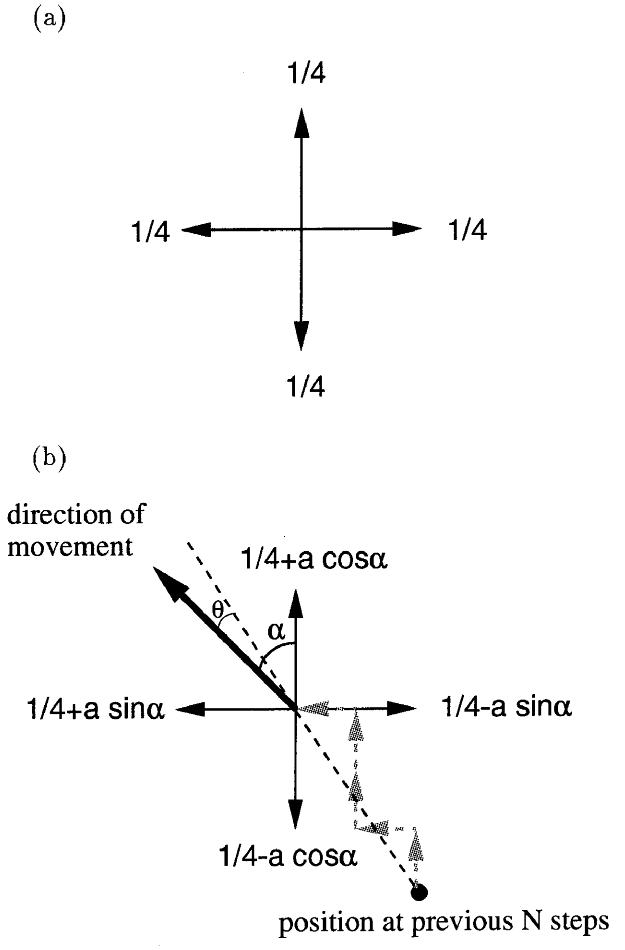


Figure 1. Schematic presentation of the model used to simulate the effect of the Lorentz force on the diffusion-limited aggregation.

2.2 Ionization Tendency

Second, in the experiment under different ionization tendency, the force is generated by a gradient of concentration of ions, because with bigger ionization tendency metal melts more from the initial germ. In the copper metal in nitride silver solution case, ionization tendency of copper ion is bigger than silver ion. Consequently, copper metal melts and a gradient of concentration happens. Figure 2 shows the present model of probability of under different ionization tendency. The particle tends to move to the initial germ.

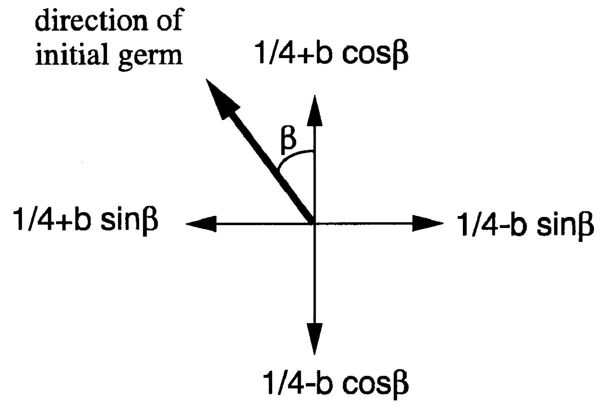


Figure 2. Schematic presentation of the model used to simulate the effect of ionization tendency on the diffusion-limited aggregation.

2.3 Coulomb Force

Thirdly, since in electrochemical deposition, the force is generated by Coulomb force, the ion in the solution is attracted to the grown crystal which contacts biased electrode. Figure 3 shows the assumed effect of the Coulomb force in the present model. Although the Coulomb force is long range, the cut-off length is assumed to be 12 sites in the present simulation. The influence of this assumption, however, is irrelevant to the main result.

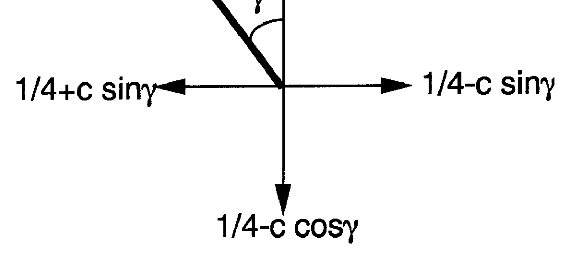


Figure 3. Schematic presentation of the model used to simulate the effect of Coulomb force on diffusion-limited aggregation.

The initial germ is set at the center of the simulation space. For description of the distance of initial ion and entire arrangement, see e.g. reference [1], because the present model is based on the DLA model. In the present simulation, when the particle arrives to contact with the crystal, it sticks permanently and a sticking probability between the ion and the crystal is 1.

3. Results

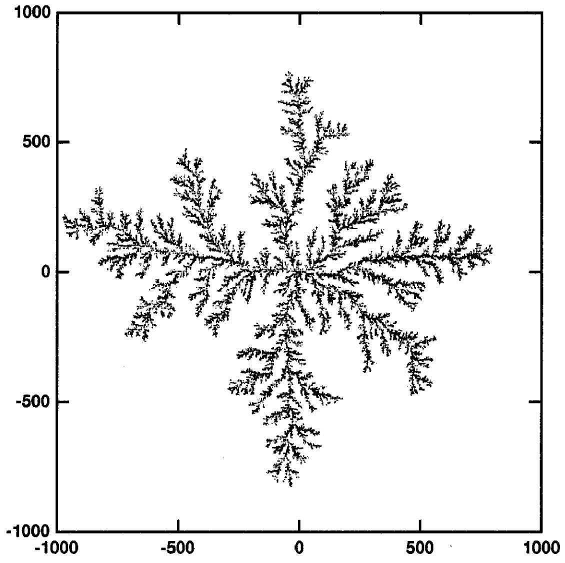
Numerical simulations were performed based on the models described in the preceding section. Typical growth patterns obtained by the present research are indicated in Fig. 4 together with the experimental results [9]. The numbers on the axes show the mesh points and therefore the sizes of the model clusters. Figure 4 (a) shows a pattern of standard DLA simulation and Fig. 4 (b) shows corresponding experimental result. By the standard DLA growth model, the well-known pattern with the fractal dimension of 1.67 is obtained.

The pattern of Fig. 4 (c) indicates a numerical result with the effect of the Lorentz force. By the simple modification of movement described in the previous section, we obtained a completely different pattern with circular deformation from the standard DLA growth. Each branch of the cluster bends and becomes thick with a slight change of the particle motion.

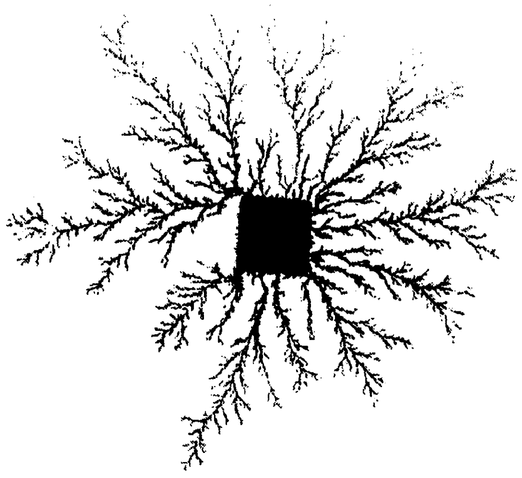
Figure 4 (d) shows the experimentally observed crystal pattern under high magnetic field [9]. This figure bears resemblance to the present simulation from the view point of the bending of the pattern. However, the number of the branches and the emvelope shape which is almost circular in experiment can not be reproduced. We, therefore, additionally assume the effect of the gradient of concentration of ion to create this pattern. Figure 4 (e) shows the simulation result including the effect of the Lorentz force together with the gradient of concentration of ions. This figure is basically similar to the pattern of the experimental result in Fig. 4 (d). The numbers and the thickness of the branches in Figs. 4 (d) and (e) are still different because of the small size of the simulation. If we can perform larger scale simualtion, the number of branches increases and accordingly the branches become thinner. In other word, Fig. 4 (d) shows a dense branching morphology (DBM), which we want to explain the result under high magnetic field. DBM is characterized by a large number of branches advancing behind a smooth stable envelope. This pattern formation in the growth of bacterial colonies has received considerable interest, both by experiment and computer simulation [14].

We also consider the effect of electric field. Figure 4 (f) shows the pattern obtained with electric field introduced in **2.3**. This figure shows a very stringy shape and is not similar to the experimental result in Fig. 4 (d).

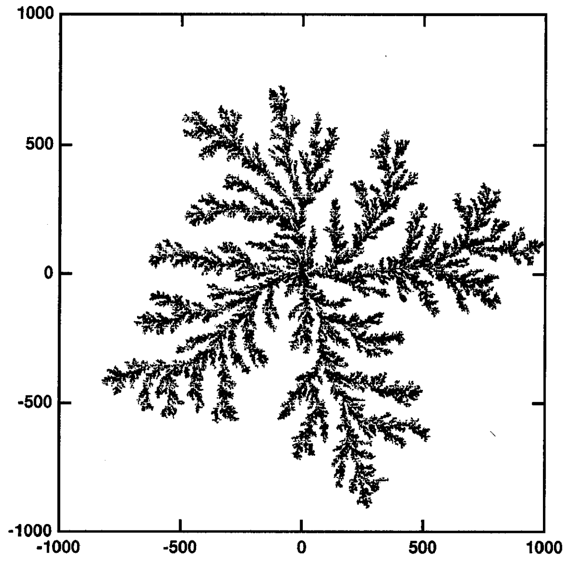
(a)



(b)



(c)



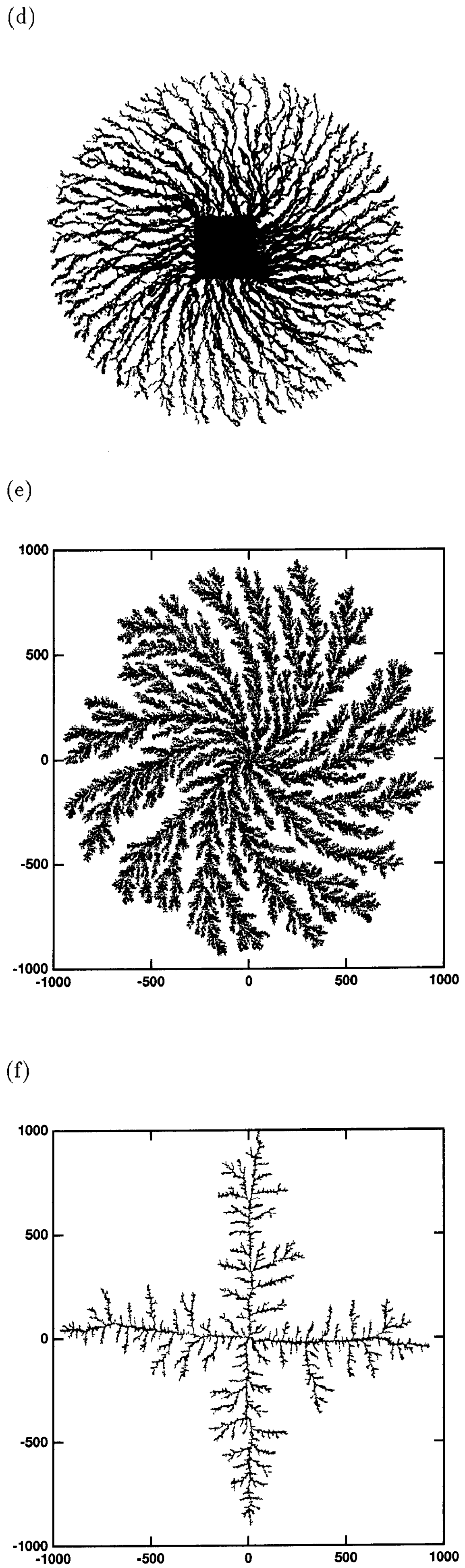


Figure 4. Typical clusters grown by simulations by applying the models in Figs. 1, 2 and 3, and described in the text and experimental results [9]. (a) Simulated pattern of the standard DLA model. (b) Observed pattern of silver leaves under 0T. The square at the center of the metal leaf is a piece of copper metal [9]. (c) Simulated crystal growth with a = 1.4 and θ = 10°. (d) Observed pattern of silver leaves under 8T. The magnetic field was applied perpendicular to the plate [9]. (e) Simulated crystal growth with the effect of the Lorentz force and the gradient of electrolyte concentration. The conditions are a = 1.0, and θ = 10 ° and ionization tendency parameter b=0.035. (f) Simulated crystal growth including the effect of Coulomb force. The effect parameter of Coulomb force is 0.7.

The fractal dimensions for various cases are evaluated from the relation, N(R) $\sim R^{D_f}$, where R is the distance from the initial germ to the crystal, and N(R) the number of particle at distance R. The obtained values of D_f are shown in Fig. 5 for various conditions.

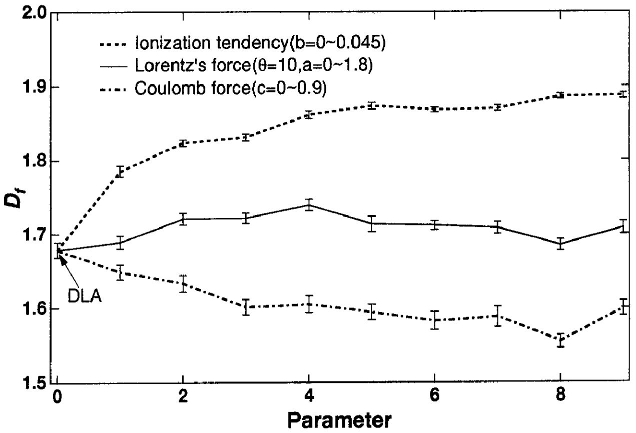


Figure 5. Fractal dimensions D_f under three conditions are shown as functions of environment parameters.

The fractal dimensions are increased by the effect of ionization tendency and decreased by the effect of Coulomb force. The effect of ionization tendency lengthens the mean free path and consequently the model aquires the ballistic nature. In the ballistic model, the fractal dimension is the same as the Euclidean dimension of the space. In the case with Coulomb force effect, strong decrease of the number of brances results in decrease of fractal dimension. According to the computer simulation of Uwaha *et al.* in terms of a lattice-gas model [15], an aggregation pattern depends on the diffusion length. The results of the present model are all consistent with a relationship between D_f and mean free path of diffusive particle presented previously by other researchers [18].

4. Discussion

Understanding the transfer processes of crystal growth has led to widespread interest from the technological point of view. Let us pick up two points, which are not solved in the present paper. First, a curve of the branch of the metal leaf [9] – [13] is a problem that should not be ignored. If the convection exists in the system, the branch of the metal leaf bends. If the pattern of the convection effect is investigated, these results [16] [17] show that the branches have a spiral form. The observed metal leaves are not spiral, and the curvature is uniform. Therefore, we propose the effect of Lorentz force in crystal growth process. The present results suggest that the effect of the Lorentz force is predominantly to change the movement of the ion under high magnetic field. Second problem is that the pattern of crystal has a round shape. The pattern created by biased ions is studied by Kim *et al.* [18]. The main result of their study is that if diffusing particles are biased to the center of system, the obtained patterns are entirely circular.

Another interesting extension consists in modifying the mean free path of the diffusing particle. In the DLA model, the mean free path is the only measure of distance between sites. In many aggregation processes in gas phase or diluted solution, the mean free path is a very important parameter, and crossover phenomena are expected. For example, if the mean free path is infinity, the regime is ballistic and the particles move on directed straight line in space randomly. The mean free path and the behavior of particles are expected to contribute a dramatic effect on the aggregation pattern. In the present model, the size of cyclotron motion is assumed to be 20 sites.

On the other hand, the environment is thought to be a diffusion-controlled process. As a result, the standard and perturbed DLA models give completely different morphologies in the final crystals. These results suggest that we are able to achieve patterns and structures in crystals by diffusion controlled processes.

5. Conclusions

Using a Monte Carlo simulation, the pattern of metal leaf growth under high magnetic field is evaluated. The results are presented by comparing the patterns between the standard and perturbed DLA models arising from various environments. The effect of the magnetic field is included by simply changing the probability of the movement perpendicular to the Monte Carlo movement. We have found that this model builds wide variety of patterns and fractal dimension is varied. Although the size of particles in the actual experiment is quite different from the one used in the present computer simulation, the fundamental behaviors of observed patterns are well explained, and the fractal dimension is also reproduced.

The model can further be extended by considering the forces between multi-particles [19], to simulate the effect of electrolyte concentration in electrochemical deposition. It is expected that the simulation of applied voltage effects would then become possible, allowing thus a more realistic representation of the experimental observations [2] [3].

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1) T. A. Witten and L. M. Sander, Phys. Rev. Lett. **47**, 1400 (1981).
2) M. Matsushita, M. Sano, Y. Hayakawa, H. Honjo and Y. Sawada, Phys. Rev. Lett. **53**, 286 (1984).
3) D. Grier, E. Ben-Jacob, R. Clarke and L. M. Sander, Phys. Rev. Lett. **56**, 1264 (1986).
4) D. Grier, D. A. Kessler and L. M. Sander, Phys. Rev. Lett. **59**, 2315 (1987).
5) P. Meakin, Phys. Rev. A **27**, 1495 (1983).
6) P. Meakin, Phys. Rev. B **28**, 5221 (1983).
7) R. M. Brady and R. C. Ball, Nature **309**, 225 (1984).
8) Y. Sawada, A. Dougherty and J. P. Gollub, Phys. Rev. Lett. **56**, 1260 (1986).
9) I. Mogi, S. Okubo and Y. Nakagawa, J. Phys. Soc. Jpn. **60**, 3200 (1991).
10) I. Mogi, S. Okubo and Y. Nakagawa, J. Cryst. Growth **128**, 258 (1993).
11) I. Mogi, M. Kamiko, S. Okubo and G. Kido, Physica B **201**, 606 (1994).
12) I. Mogi, M. Kamiko and S. Okubo, Physica B **211**, 319 (1995).
13) I. Mogi and M. Kamiko, J. Phys. Soc. Jpn. **64**, 4500 (1995).
14) E. Ben-Jacob, A. Tenenbaum, O. Shochet and O. Avidan, Physica A **202**, 1 (1994); E. Ben-Jacob, O. Schochet, A. Tenenbaum, I. Cohen, A. Czirók and T. Vicsek, Nature **368**, 46 (1994); M. Ya. Azbel, Europhys. Lett. **22**, 311 (1993).
15) M. Uwaha and Y. Saito, J. Cryst. Growth **99**, 175 (1990).
16) T. Nagatani and F. Sagués, J. Phys. Soc. Jpn. **59**, 3447 (1990).
17) L. López-Tomás, J. Claret, F. Mas and F. Sagués, Phys. Rev. B **46**, 11495 (1992).
18) Y. Kim, K. R. Choi and H. Pak, Phys. Rev. A **45**, 5805 (1992).
19) H. Mizuseki, K. Kikuchi, K. Tanaka, K. Ohno and Y. Kawazoe, to be published.