Structure transition in cluster-cluster aggregation under external fields

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The structure transition in cluster-cluster aggregation (CCA) under different external electric fields has been investigated by computer simulations. The aggregates are generated from off-lattice CCA models involving the field-induced dipolar interactions and temperatures by means of a Metropolis algorithm. When the parameter K increases from 0 to ∞, the clusters gradually change from a diffusion-limited CCA to a chainlike pattern, where K stands for the relative strength of the field-induced dipolar interaction with thermal energy. The relation of fractal dimension D_f to parameter K can be approximately expressed as $D_f = D_E + (D_{DLCA} - D_E)e^{-\beta K}$ with $\beta = 0.64$, where D_E and D_{DLCA} stand for the fractal dimensions of the CCA when $K \to \infty$ and $K \to 0$, respectively. This structure transition is a transition between a prototype disorder structure and a relative order one. The transition is attributed to the variation of the dominating interaction of systems from thermal disorder to field-induced dipolar interaction with K rising.

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I. INTRODUCTION

Fractal growth and aggregation phenomena have attracted considerable interest in the last two decades [1–16]. The structure of aggregation strongly depends on the dynamics of the growth process. Many computer simulations have been carried out to investigate the relationships between the geometry and the mechanism. Great efforts have been directed toward the development of models for fractal growth and aggregation processes. There are two basic models of fractal aggregation: diffusion-limited aggregation (DLA) [1–4,13–16] and cluster-cluster aggregation (CCA) [4–8]. In particular, numerical simulations performed with the CCA model can describe the fractal structure of aerosols and colloids [12], which is in good agreement with experimental results. In a diffusion-limited CCA model, particles are driven by diffusion and they only experience short-range interactions such as the hard-core interaction [2,4–8].

Several authors have extended the DLA model in order to take interparticle interactions into account [3,13–16]. Block *et al.* presented a model of deterministic DLA in which particles do not undergo Brownian motions. Instead, they undergo a deterministic trajectory under a power-law force exerted by the particles already attached to a cluster [15]. Pastor-Satorras and Rubi introduced a model of DLA with dipolar interaction, in which dipolar interaction was considered by means of a Metropolis algorithm [16]. But for the CCA model, long-range interaction between particles is seldom considered [2,4–8].

In this paper, we have studied the CCA model under external electric fields using Monte Carlo off-lattice simulations. The effect of an electric field is introduced by a Metropolis algorithm like those in Refs. [16–18]. The results will be useful to the understanding of the characteristics of the CCA model, as well as colloid aggregation under different external fields.

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II. MODEL AND SIMULATIONS

The system in this work is a square cell, in which particles are placed. The cell is under an external electric field $\mathbf{E}_0$. The diameter σ of particles is chosen as the unit of length. The model used is very similar to the off-lattice CCA model [2,8,19], except that the field-induced dipolar interaction between particles is introduced by means of a Metropolis algorithm like those in Refs. [16–18].

A particle under an electric field is polarized, and it has an induced dipole moment [20,21]

$$\mathbf{p} = \alpha\sigma^3\mathbf{E}_{\mathrm{loc}}, \tag{1}$$

where σ is the diameter of the particle. $\mathbf{E}_{\mathrm{loc}}$ is the local electric field and α is related to the dielectric properties of the particle and the surrounding medium. The dipolar interaction between the i and j particles, located at the positions $\mathbf{r}_i$ and $\mathbf{r}_j$, respectively, is given by the energy [16,17,20]

$$U_{ij} = p^2 u_{ij}, \tag{2a}$$

where $p = \alpha\sigma^3 E_0$. u_{ij} is the dimensionless field-induced dipolar energy

$$u_{ij} = [\mathbf{p}_i^* \cdot \mathbf{p}_j^* - 3(\mathbf{p}_i^* \cdot \mathbf{r}_{ij})(\mathbf{p}_j^* \cdot \mathbf{r}_{ij})/\mathbf{r}_{ij}^2]/\mathbf{r}_{ij}^3, \tag{2b}$$

where $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j \cdot \mathbf{p}_\mu^* = \mathbf{p}_\mu / p$ with $\mu = i, j$.

We start the simulations with random particles in a cell that is placed under an electric field. Every particle experiences the interactions exerted by other particles. Suppose that the system is composed of N particles. The total energy is given by

$$U = \sum_{j=1, j\neq i}^{N} u_{ij}. \tag{3}$$

For a cluster (including a single-particle cluster) after a Monte Carlo time step, we compute the new position. The cluster arrives at the new position by means of a Brownian motion, i.e., the particles in the cluster jump to the circle

centered on themselves in the same direction, which is chosen randomly [8]. The radius ρ of the circle is taken as follows in our simulations:

$$\rho=\begin{cases} 1, & d\geqslant d_0, \\ d/d_0+\delta, & d<d_0, \end{cases} \tag{4}$$

where d is the minimum distance between this cluster and other clusters. d_0 is a parameter taken as 10, which means the walk step is very small when two clusters become close to each other [19]. δ is chosen to be 0.01, which allows two particles to overlap slightly [13,14]. After the movement of the cluster, the total energy U' can be calculated. The change in total energy due to the movement is $\Delta U=U'-U$. If $\Delta U<0$, then the movement is accepted and performed. If $\Delta U>0$, we compute the quantity [16–18]

$$p_M=e^{-K\Delta U}, \tag{5}$$

where the parameter K determines the relative strength of the field-induced dipolar interaction versus the thermal energy and is presented by [16–18]

$$K=\frac{p^2}{\sigma^3 k_B T}, \tag{6}$$

where k_B and T are the Boltzmann constant and temperature, respectively. In the simulations, the cutoff radius r_0 is introduced and r_0 is chosen to be 10 [21]. In the latter case, the movement is performed with probability p_M. If two particles sticking to two different clusters overlap, then the two clusters become one cluster. In this manner, clusters grow larger and larger.

III. RESULTS

To simplify the problem, we consider a two-dimensional cell (100×100). An external electric field $\mathbf{E}_0$ is applied in the Y direction. The parameter K is chosen to be 0, 0.001, 0.01, 0.1, 0.5, 1, 2, 5, 10, 100, and 1000, respectively. K is the parameter that stands for the relative strength of field-induced dipolar interaction versus thermal energy. Because the energy calculation is involved in the algorithm and the step is small, the algorithm can only be carried out at very low speed. The total particle number is taken as $N=1000$. Ten initial configurations are used for each case in our simulations.

Figure 1 gives the morphologies for CCA under different electric fields. From (a) to (b), K takes 0, 1, 5, and 100. It can be seen from Fig. 1(a) that when $K=0$, the aggregates appear relatively symmetrical and uniform. The branches grow in a random direction. The system presents a kind of typical fractal pattern. It is a kind of prototype disorder structure (diffusion-limited CCA). If $K\neq0$, the aggregates appear partial to the $\mathbf{E}_0$ direction. The branches prefer to grow along the $\mathbf{E}_0$ direction, and the aggregates do not look symmetrical and uniform [see Fig. 1(b)]. As K increases, the anisotropy of the aggregates appears more apparent, and particles can form fiberlike structures along $\mathbf{E}_0$. But the fibers are not strictly arranged in the $\mathbf{E}_0$ direction [shown in Fig. 1(c)]. If K becomes large enough, the CCA changes into a chainlike structure along the direction of $\mathbf{E}_0$, which can be seen from Fig. 1(d). The structure is an order structure resulting from strong field-induced dipolar interaction, which is very similar to that of the well-known electrorheological fluids [21].

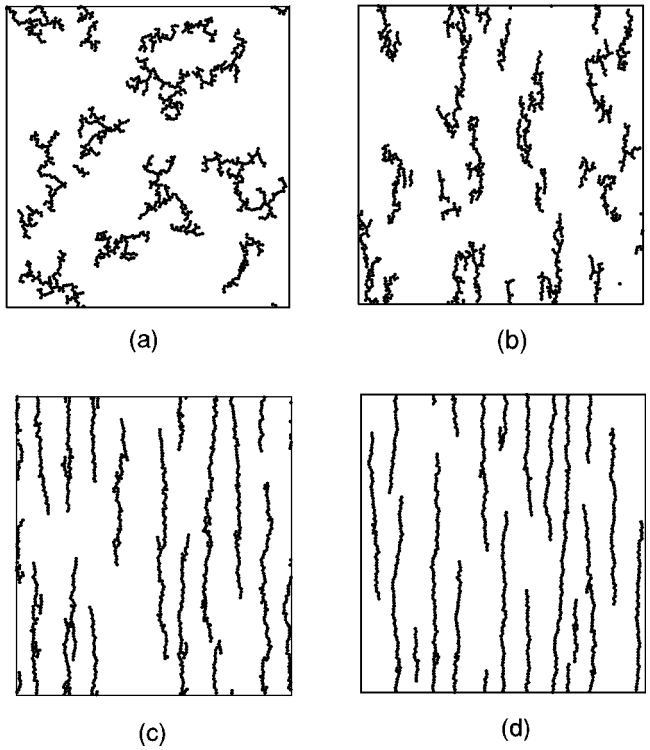

FIG. 1. Morphologies for cluster-cluster aggregation with different K, $N=1000$: $K=0$ (a), 1 (b), 5 (c), and 100 (d). The external electric field is applied in the Y direction.

The structures are also examined by using the pair-distribution function $g(r)$, which is often used in the study of liquid [22].

$$g(r)=\rho(r)/\rho_0, \tag{7}$$

where $\rho(r)$ is the density of a particle number at r and ρ_0 stands for the mean density. ρ_0 is a constant for a system. Here we use reduced pair function $g^*(r)$, which is presented by

$$g^*(r)=g(r)\rho_0. \tag{8}$$

Figure 2 shows $g^*(r)$ for $K=0$, 1, 5, and 100 from (a) to (d). We can see from Fig. 2(a) there is only a clear peak of the nearest-neighbor particles. The structure is a typical disorder one, but with order in the short range. It is very similar to those of liquids [22]. With the parameter K increasing, the range in which order exists becomes large. The next-neighbor peak and other peaks appear gradually [see Figs. 2(b) and 2(c)]. As K continues to increase, all the peaks clearly appear [shown in Fig. 2(d)]. The structure is a relative-order one that can be called a mesocrystal structure [20,23]. In Fig. 2, the departure of the peak position from 1, 2, 3, 4... is attributed to two things: one is that particles are allowed to overlap, the other is that chains of particles are not so perfect. It follows that the CCA changes from a typical disorder structure to a relative order one when the parameter K increases from 0 to ∞.

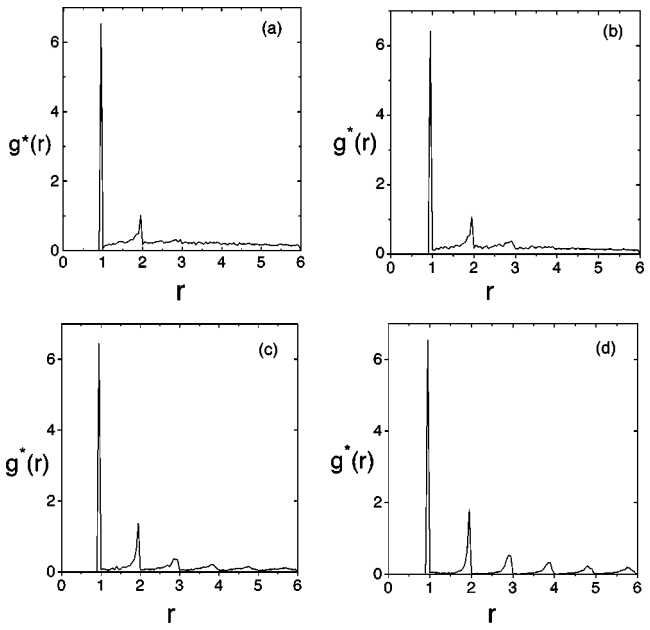

FIG. 2. Reduced pair distribution functions $g^*(r)$ of cluster-cluster aggregation versus r. $K=0$ (a), 1 (b), 5 (c), and 100 (d).

Fractal dimensions are calculated for the different aggregates by using the following equation [2,6,24]:

$$N \sim R_g^{D_f}, \tag{9}$$

where D_f is the fractal dimension. N and R_g stand for the particle number and gyration radius of a cluster, respectively. R_g can be determined by [2,13,14,24]

$$NR_g^2 = \sum_{i=1}^{N} (\mathbf{r}_i - \mathbf{r}_c)^2, \tag{10}$$

where $\mathbf{r}_c$ is the position vector of the mass center of the cluster. The D_f are plotted as a function of the parameter K in Fig. 3. It can be seen that D_f decreases with K increasing. When K changes from 0 to ∞, D_f decreases from 1.42 ± 0.03 (D_f of a two-dimensional (2D) diffusion-limited CCA) to about 1. There is a rapid decrease of D_f in the range $0.1<K<10$, and we found that the relation of D_f to the parameter K can be approximately expressed as

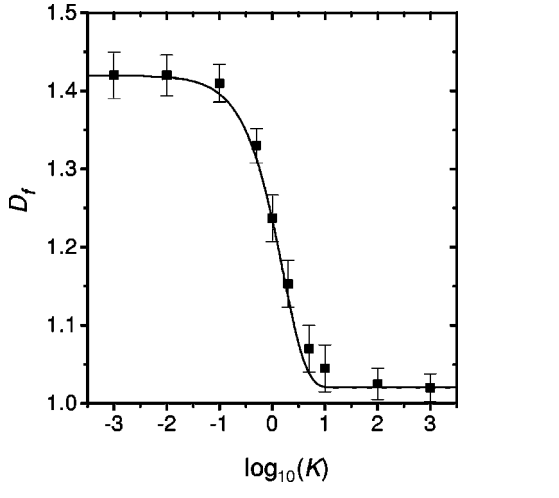

FIG. 3. The fractal dimension D_f as a function of the parameter K for cluster-cluster aggregation. The solid line is the plot of Eq. (11).

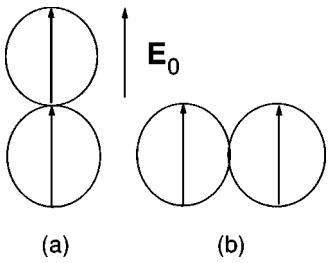

FIG. 4. Two typical positions of two couples of particles under an electric field. The external field is applied in the Y direction.

$$D_f = D_E + (D_{DLCA} - D_E)e^{-\beta K}, \tag{11}$$

with $\beta = 0.64$, where D_E and D_{DLCA} stand for the fractal dimensions of CCA when $K \to 0$ and $K \to \infty$. Here, D_E is about 1.02 and D_{DLCA} is 1.42 for the 2D cell in the simulations. In Sec. IV, we will show that the relation is reasonable.

IV. DISCUSSION

The transition in CCA under different electric fields is in essence the change from a typical disorder structure to an order one. This transition is due to the interaction between particles in the systems. Figure 4 gives the two typical positions of two couples of particles that are in the presence of an electric field. The field-induced dipolar interaction energies are $u=-2p^2$ (a) and $u=p^2$ (b), respectively, by using Eq. (2). When $K=0$, i.e., $p=0$, thermal disorder completely dominates the system. In this case, the position (a) is the same as the position (b). Particles undergo pure Brownian motion and form random branches. Therefore, the aggregates appear as typical fractal patterns (2D diffusion-limited CCA), and their fractal dimension is about 1.42. If $K \neq 0$, there exists a competition between thermal disorder and field-induced dipolar interaction. For the case of small K, i.e., small p, the system is still controlled by thermal disorder, but dipolar force has a little effect on aggregates too. Position (a) is a little superior to position (b). Thus the aggregates present fractal patterns with a little anisotropy; i.e., they look a little partial to the direction of $\mathbf{E}_0$. With rising K, the controlling interaction of the systems gradually changes into a field-induced dipolar one and position (a) is much superior to position (b). So particles prefer to aggregate along the direction of $\mathbf{E}_0$ and form fibers in the $\mathbf{E}_0$ direction. In this case, thermal disorder still exists as a perturbation, which results in fibers that are not so perfect. As for the case where K is large enough, the CCA appears as an ordered pattern of perfect chains that can be called a mesocrystal structure [20,23]. The great transition takes place in the range $0.1<K<10$. When K increases from 0.1 to 10, the dominating interaction of the system changes from thermal disorder to field-induced dipolar interaction correspondingly, which results in the rapid decrease of D_f in the range.

Now we give the explanation of Eq. (11) as follows. Consider a couple of particles: when they become neighbors, the change in-field-induced dipolar interaction is given by Δu. If $\Delta u<0$, the configuration of the couple is accepted. If Δu

$\geqslant 0$, the acceptance probability p_M is given by Eq. (5), and the mean change $\overline{\Delta u}$ of dipolar energy for the case $\Delta u \geqslant 0$ can be computed by Eq. (2). At last, we can get $\overline{\Delta u} = 0.64$ (dimensionless energy). Thus the mean acceptance probability $\overline{p}_M$ for $\Delta u \geqslant 0$ becomes $\overline{p}_M = e^{-0.64K}$. This expression shows that $\overline{p}_M$ decreases from 1 to 0 when K increases from 0 to ∞. Correspondingly, D_f decreases from D_{DLCA} to D_E. The mean probability $\overline{p}_M$ determines the space distribution of particles, which is described by D_f. We simply suppose that D_f has a linear relation to $\overline{p}_M$ and get $D_f = D_E + (D_{DLCA} - D_E)\overline{p}_M$. This is Eq. (11) precisely.

The process of colloid aggregation under certain external electric fields simulated by this model is as follows. At the beginning, the neighboring particles aggregate into small clusters. Each of them is formed under the effects of thermal disorder and field-induced dipolar interaction. Then small clusters continue to grow and congregate into larger clusters with increasing time. Similarly, the formation of the larger clusters is also affected by the same thermal disorder and dipolar interaction.

In the model, clusters are supposed to be rigid like the classic CCA model [2,5–8]. A model involving the deformation of clusters is a more physical one used to describe the aggregation dynamics process. Especially for the aggregation under an increasing external field, the clusters formed under a low external field should be deformed and form chains for the higher external field.

V. CONCLUSION

The influence of the external electric field on the structure of CCA has been studied by Monte Carlo simulations. It shows that the Metropolis algorithm is an effective method for studying the system having competition between thermal disorder and another interaction. For the CCA under an external field, with the external electric field rising, the pattern changes from a typical disorder structure (diffusion-limited CCA) to an order one (chainlike). The expression of the fractal dimension to the parameter K is obtained. The transition is attributed to the variation of dominating interactions of the system from thermal disorder to field-induced dipolar interaction.

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