Simulation of Diffusion-Limited Aggregation and Reactions over Its Surfaces

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Abstract

Modifications of Witten–Sander diffusion-limited aggregation (DLA) were proposed. Effects caused by releasing boundary shape, nonfixed seed, and rotating biased drift on the morphology of the resulting DLA were examined. The diffusion-limited reaction on surfaces of DLA were also studied by performing a multifractal scaling analysis. © 1994 John Wiley & Sons, Inc.

I. Introduction

Witten–Sander diffusion-limited aggregation (DLA) and its fractal nature have been extensively studied [1–10] since it first was reported in 1981 [11]. Factors affecting the DLA processes were examined quite thoroughly and several versions of the DLA model were suggested [12–15]. Even though the model is still not well understood from a fundamental point of view, it has been used successfully to describe a wide range of nonequilibrium growth processes including electrodeposition [16, 17], dielectric breakdown [18], fluid–fluid displacement processes [19, 20], the dissolution of porous materials [21], random dendritic growth [22], and a variety of biological growth processes [23–26]. In this article, we address some interesting findings concerning simulations of DLA and diffusion-limited reaction (DLR) over DLA surfaces.

In most studies on DLA and on similar random-aggregation models, the particle is released one at a time from a circular boundary far enough from the fixed seed and then it walks in a pure stochastic way. Because the simulations were frequently performed on finite, discrete lattices, the equal-distance circular boundary is not an equal-event boundary. The effect caused by the releasing boundary shape was examined and a modified DLA model was proposed in which the particle is released from a diamond-shaped boundary on a square lattice. Applying the modified DLA model, effects caused by nonfixed seed and rotating, biased drift on the DLA pattern were examined. The reactivity of the DLA was then studied by performing a Monte Carlo simulation of the DLR on DLA surfaces. It is found that single fractality is not able to describe the reaction probability distribution for the DLR on DLA surfaces. A multifractal scaling technique was applied to analyze the dispersion relation of the fractal dimensionality for the probability distribution of reaction occurring on DLA surfaces.

This article is composed as follows: Methods and models are briefly stated in Section II. Effects caused by the releasing boundary shape and nonfixed seed are presented in Section III. The influence induced by the biased drift on the DLA pattern is presented and discussed in
Section IV. The DLR over DLA surfaces is analyzed using a multifractal scaling technique and is discussed in Section V. Concluding remarks are given in Section VI.

II. Methods and Models

Quantitative measure of the fractal attribute in a process is generally represented by a critical index, $D$, which is defined by the following relation [5, 9]:

$$M(aL) = a^D M(L),$$  

(1)

where $D$ is the fractal dimensionality and is always smaller than the Euclidean dimension. For DLA, $M$ is simply the mass and $L$ is the gyration radius. The fractal dimensionality is one of the important indices in the simulation of DLA and related processes.

Recently, we constructed a modified version of the Witten–Sander model for DLA for the sake of saving computing time [27]. In this modified version, acceptable radii of the releasing boundary, $R_i$, and the outer boundary, $R_o$, are adopted to optimize the cluster growth rate and to minimize the CPU consumption. As the cluster grows, the radii of the inner and outer boundaries expand accordingly. The relationship among the radii of the cluster, $R_m$, the releasing boundary, and the outer boundary are kept as $R_m : R_m + R_i : R_m + R_o$ during the simulation, where $R_m$ represents the maximum radius in the growing cluster. In our simulations, the initial radii of the releasing boundary $R_i$ and outer boundary $R_o$ were taken to be 24 and 36 units of the lattice constant.

In the conventional DLA model, a seed is fixed at the center of the square lattice. Particles are released one at a time from a randomly selected point on a circle that is centered at the seed. The selected particle then undergoes a random walk on the lattice until it either reaches an empty site neighboring the growing cluster or it goes out of the outer perimeter and is discarded. In these models, the simulations were frequently performed on a finite, discrete lattice. The circular releasing boundary is not an equal-event boundary, namely, the releasing sites on the circle are of different steps away from the seed. A set of releasing sites with an equal-step away from the seed constructs a diamond-shaped boundary as shown in Figure 1. For simulations on a triangular lattice, the equal-distance and equal-event boundaries are also presented in Figure 1. In this article, we report the effect of such a difference on the DLA.

The second effect that we report is the effect caused by the nonfixed center of the releasing boundary. In simulating this effect, we performed the modified DLA model where the center of the releasing boundary is initially located at the seed site. However, during the growing process, a new releasing center is chosen at random to be any site in the growing cluster whenever a new particle is going to be released from a releasing boundary. Note that the radii of the inner and outer margins from the new seed are kept fixed. Here, the particle is discarded only when its distance to each particle in the growing cluster are all greater than the radius of outer perimeter. A new center is then reset and a new particle is released to start the growing process over. The effect caused by the nonfixed seed option will be discussed and examined.

The third effect that we report is the effect caused by a certain biased drift. The biased random walk (BRW) on a square lattice is defined in the following way: For a particle that originally sits on a lattice point $(a, b)$ in region I where $a > b$ (see Fig. 2), the probabilities for this particle to hop to its four nearest neighbors at the next Monte Carlo step are given
by the following equations:

\[
P(a - 1, b) = \frac{1 - \alpha}{4} + \left(\frac{F_c}{F_c + F_r}\right)\alpha \\
P(a, b - 1) = \frac{1 - \alpha}{4} + \left(\frac{F_r}{F_c + F_r}\right)\alpha \\
P(a + 1, b) = \frac{1 - \alpha}{4} \\
P(a, b + 1) = \frac{1 - \alpha}{4}
\]
The axial component, \( F_a \), and tangential component, \( F_t \), of the attractive force, \( F \), between the seed and the incoming particle in regions I and II are shown. Some typical trajectories of particles in the case of \( F_t = 0 \) are also shown.

\[
0 \leq \alpha \leq 1 ,
\]

(6)

where \( P(i, j) \) is the probability for the particle to hop form \((a, b)\) to \((i, j)\); \( \alpha \) is a tuning parameter; and \( F_a \) and \( F_t \) are, individually, the axial and tangential component of the biased drift, \( F \), the attractive force between the seed of cluster and the incoming particle as indicated in Figure 2. The pattern of the resulting cluster can be controlled by tuning \( \alpha \) and the \( F_t/F_a \) ratio. Two limiting cases where \( F_t/F_a \to 0 \) or \( \infty \) will be reported and discussed here. For the general discussion concerning this part, one might refer to [28].

In simulating the DLR over the DLA, a 2-D DLA was first grown on a square lattice using the above-mentioned modified Witten–Sander model in which the particles were released one at a time from an equal-event boundary, i.e., a diamond-shaped boundary [27, 29]. As the DLA grew to a certain size, the releasing particle was changed to the reacting species. The released particle then underwent a random walk on the checkboard until it either reached the surface site of the DLA cluster or it detoured a long distance on the lattice until it went out of the outer perimeter. Once a reacting particle collided with a surface site, the reaction counts on that surface site were added by one. After a large enough number of particles were launched, the reaction probabilities of different surface sites were recorded and analyzed. Multifractal analysis has been proven to be useful in the study of processes in environments of complex geometry, for instance, in the scaling analysis of the aggregation probability distribution of fractal objects [30–32]. In our case, the fractal set of surface active sites of a DLA can be divided into subsets where each subset is characterized by its own reaction probability distribution and its own fractal dimension.
The essence of the multifractal analysis is briefly stated as follows: For details, one might refer to the review article by Halsey et al. [33]. For a given probability distribution, its \(q\)th-order moment, \(M_q\), and the scaling exponents, \(\tau(q)\), can be defined as

\[
M_q = \sum_i p_i^q = \sum_p n(p)p^q \propto L^{-\tau(q)},
\]

where \(p_i\) is the reaction probability of site \(i\); \(n(p)\), the number of sites with reaction probability \(p\); and \(L\), the linear size of the fractal object, i.e., the average radius of DLA. In the limiting case of large \(L\), the following scaling assumptions were used [30,33]:

\[
p(q) \propto L^{-\alpha(q)}
\]

\[
n[p(q)] \propto L^f(\alpha),
\]

where \(p(q)\) denotes the value of \(p\) that dominates the sum in Eq. (7) for the \(q\)th-order moment. Substitution of Eqs. (8) and (9) into Eq. (7) gives the equivalent relation

\[
\tau(q) = q\alpha(q) - f(\alpha).
\]

The value of \(\alpha\) is then computed by

\[
\frac{d}{dq} [\tau(q)] = \alpha(q).
\]

Evidently, if a linear \(\tau\) vs. \(q\) plot is found, the system is characterized by only one pair of \(\alpha\) and \(f(\alpha)\), namely, by one single fractal dimension. Therefore, a nonlinear \(\tau-q\) curve implies the multifractality feature characterizing a system.

As mentioned earlier, we apply the multifractal scaling that relates to the analysis of a distribution of an entity, the reaction probability in our case, over a volume, the size of the DLA cluster here. Similar treatments have been introduced for different systems, such as the scaling properties of molecular spectra [34], the nature of the wave functions in the Anderson model [35], and fluctuations in transmission lines [36]. For our analysis, the sizes of DLA were chosen to be 1000, 3000, and 10,000, whose average radii were equal to 45, 87, and 170 lattice units, respectively. The fractal dimensions of these three DLA are \(1.71 \pm 0.02\). The inner radius of the releasing boundary was chosen to be 12 units away from the maximum radius of the cluster. All simulations were terminated after 100,000 reaction events occurred.

III. Effects of Launching Boundary Shape and Nonfixed Seed

To demonstrate the effect of the releasing-boundary shape on DLA, we first performed the modified Witten–Sander model on a \(700 \times 700\) square lattice with a circular releasing boundary. A diamond-shaped aggregate resulted. The reason for the anisotropic contour might be rationalized, as we pointed out earlier that not every site on the circular boundary is an equal-event site. A typical DLA of our modified Witten–Sander model using a square releasing boundary has a relatively less anisotropic cluster since all the particle-releasing sites on a square boundary are equal-event sites. A second difference between these two configurations with equal radius is that particles launched from circular boundary have larger probabilities to stay inside and will squander much random walk time owing to its clumsy occupancy of lattice sites (here the radius for square boundary is the steps away from its center). Hence, particles projected from the square margin have the prevailing chance to adhere to the cluster
and thus better aggregation efficiency with respect to those released from a circular margin. The effect of boundary shape on DLA can also be found in simulations on any finite, discrete lattice. For instance, on a trigonal lattice, the equal-step sites form a hexagonal boundary as shown in Figure 1. However, the effect on the shape of the resulting DLA is less pronounced on a trigonal lattice. This can be easily understood since a regular polygon would get closer and closer to a circle as the number of edges increases.

The effect of boundary shape on DLA is caused mainly by the finite, discrete lattice used in the DLA simulation. In a semilattice or off-lattice simulation, this effect can be lowered. Also, if the noise reduction parameter or the mean field parameter is increased, the resulting DLA is exactly the same no matter what boundary is used [37].

For two-dimensional DLA with nonfixed seed, simulations were also performed on a 700 × 700 square lattice. The impetus behind this model is to fabricate a cluster with continuously changing fractal dimensionality and to find the variation of cluster patterns. By analysis of the fractal dimensionality of the growing cluster at different cluster sizes, we found that the fractal dimensionality was changing continuously [27]. This observation can be rationalized in the following way: Due to the randomness of the seed site, the screening effect in the fixed-center DLA simulation is diminished, namely, the interior core of the growing cluster is filled up gradually during the growing process. The limiting cases in both directions might be viewed as a cluster with a compact interior when extrapolated to an infinite large cluster size and a cluster with no chance to attach to the interior core when extrapolated to zero cluster size. The former is analogous to an Eden cluster, whereas the latter is a Witten–Sander DLA. The

![Figure 3. The fractal dimensionality analyzed as every 2000 particles were added to the growing cluster in 2d simulations of the moving-center model where solid circles and open squares stand for square and circular releasing boundaries, respectively.](image-url)
changes of fractal patterns with fractal dimensionality of our second model in two-dimensional simulations are illustrated in Figure 3, as we plotted the fractal dimensionality as a function of cluster size. This model has built a way from the Witten–Sander DLA to the Eden model. Our second model somehow displays the same features that were achieved by the simulations using Levy flight trajectories [38]. The continuously changing fractal dimensionality as the DLA cluster grows gives us a clue as to how to generate a DLA having fractal dimensionality somewhere between 1.67 and 2 if we combine the fixed-center model and nonfixed-center model in an appropriate weighting ratio. We display in Figure 4 a series DLA generated in the way that we just described. As can be seen from Figure 4, the fractal dimensionality in each cluster is found to vary continuously as the weighting ratios of fixed to nonfixed model change form 10:0 to 9:1 to 0:10.

Finally, the fractal dimensions obtained from the simulations of our first model in two-dimensional simulations are found to be in good agreement with previous experimental works [39, 40] and theoretical calculations [14, 41, 42]. A square releasing boundary in two-dimensional simulations seems to be a more efficient way to generate larger clusters instead

![Figure 4](image-url)

Figure 4. The resulting 3000-site DLA clusters generated from an algorithm combines fixed DLA and nonfixed DLA with a weighing factor of (a) 10:0, (b) 7:3, (c) 3:7, and (d) 0:10.
of the conventional circular one without changing the fractal characteristics. The nonfixed seed DLA model displays a continuously changing fractal dimensionality as the cluster grows and it provides a clue as to how to develop a model to generate a DLA cluster with fractal dimensionality between 1.67 and 2.

IV. Effect of Biased Drift

To demonstrate the effect of biased drift on DLA, the movement of the particle is simulated via a biased random walk (BRW) algorithm according to hopping probabilities described in Eqs. (2)–(6). As mentioned earlier, the DLA pattern can be controlled by the fine tuning of $\alpha$ and the $F_r/F_c$ ratio. Two limiting cases where the $F_r/F_c$ ratio equals zero or $\infty$ are presented here. For details, one might refer to [28].

In the case that the tangential component, $F_r$, of the biased drift is neglected or $F_c \gg F_r$, the probability of particle hopping in BRW is changed into Eqs. (12)–(14):

$$P(a-1,b) = \frac{1-\alpha}{4} + \alpha$$  \hspace{1cm} (12)

$$P(a,b \pm 1) = \frac{1-\alpha}{4}$$  \hspace{1cm} (13)

$$P(a+1,b) = \frac{1-\alpha}{4}$$  \hspace{1cm} (14)

which is, in fact, the same as those of the Kim–Choi-Pak (KCP) model [43]. Thus, neglect of the tangential component simply reproduces the KCP model. In the limiting case of $\alpha = 1$, the particle released from position $(a,b)$ in region I will eventually reach position $(b,b)$ after hundreds of Monte Carlo steps because the axial component, $F_c$, which is parallel to the $x$-axis, is dominating in this region. After the particle reached $(b,b)$, at the diagonal, the particle moves in a zigzag way from $(b,b)$ to the seed, i.e., $(b,b) \rightarrow (b-1,b) \rightarrow (b-1,b-1) \rightarrow (b-2,b-1) \rightarrow \ldots \rightarrow (0,0)$ as displayed in Figure 2. Therefore, the configuration of the cluster is "$x$"-shaped because of the peculiar path of the incoming particle. A set of typical clusters obtained from this set of simulations is presented in Figure 5. As Figure 5 shows, the cluster shape is changed from thinner "$x$"-shape to the thicker one as the $\alpha$ value is decreased. As the $\alpha$ value is less than 0.005, the shape looks more like the ordinary DLA and the fractal dimension is estimated to be $1.69 \pm 0.02$. However, it is still believed that, for the nonzero $\alpha$, no matter how small the $\alpha$ value is, if the $R_{in}$ is large enough, the cluster shape of KCP model should be "$x$"-shaped.

On the other hand, in the simulation of the zero $F_r$ component, a set of different kinds of clusters possessing basically a "+" shape, i.e., axially elongated, is created. Typical examples of this set of clusters are shown in Figure 6. As the $\alpha$ value increases and only the $F_r$ component exists, the incoming particle has a better chance to hop to the axial direction. In the limiting case of $\alpha = 1$, no cluster will be obtained because the incoming particle will waste all the time back and forth around the axial sites. It is interesting to note that this result reproduces the effect of larger noise reduction parameter on DLA [44]. Obviously, increase of the noise reduction parameter consumes much more CPU time than our model does. For the cases between these two limits, i.e., $F_r/F_c$ equals a finite value, DLA clusters with mixed axial and diagonal lobes are generated [28].
V. Multifractal Scaling of DLR over DLA Surfaces

The reaction events that occurred at each site on the DLA surface were recorded by counting the number of visits by the reacting particles. According to the event occurrence, the sites in a DLA were divided into three different sets: The first one is a set of inactive sites, i.e., the sites within the core region of DLA, which cannot be reached because they are surrounded by four nearest neighbors. The second one is the set of screened active sites, i.e., the inner surface sites, where no visits by reacting species were observed during the simulation. The third one is the set of active sites, i.e., the outer surface sites. Increase of the DLA size affects the distribution of the number of sites of each set. The number of inactive sites within the core increases as the average radius ($L$) of DLA increases. The number of screened active sites raises even more quickly as the DLA size increases, namely, the screening effect is becoming much more pronounced. Unlike those for Devil’s Staircase (DS) and Cantor Set (CS) where the population of each kind of sites is predetermined, both inactive sites and screened sites are produced in a relatively random way in a DLA.

To understand the position sensitivity of the reaction probability, the reaction probability is plotted as a function of active site position for the DLA in Figure 7, where the active sites are numbered from inner part of DLA outwardly. For active sites of the same radius, they are numbered clockwise. Note that the inactive sites and the screened active sites are not included in this plot. As the DLA size decreases, the range of the reacting probability has a
Figure 6. A set of typical clusters obtained from BRW simulations with $F_c = 0$ and (a) $\alpha = 0.1$, (b) $\alpha = 0.05$, (c) $\alpha = 0.01$, and (d) $\alpha = 0.005$. The cluster sizes are all equal to 200 lattice units.

wider distribution, showing a higher position sensitivity. It can be seen in Figure 7 that the number of low reacting probability sites gradually increases as the DLA size increases. The spike-shaped distribution shows that certain sites were rarely visited due to the depth screening effect, i.e., the screening of inner active sites by the outer ones. In Figure 8, $\tau$ is plotted as function of $q$ for 1000-, 3000-, and 10,000-particle DLA clusters. The $\tau-q$ relation is not linear, indicating that simple single-valued fractal scaling does not apply in this condition. Similar behavior was also found in CS and DS by Avnir et al. [45]. The multifractal pattern is parallel to DS as the size of the DLA increases. However, a difference can be observed in the parts of high negative $q$ values. In the case of DLA, it shows a bigger deviation from a full superposition of the $\tau-q$ curve as the radii increase. This result can be explained by the fact that the number of active sites with the lowest reacting probability $[p(q)]$, which dominates the sum in Eq. (7) at large negative $q$, are quite different in three different sizes of DLA. In Figure 4, the reaction probability distribution (RPD) of DLA also shows a stronger multifractality as compared to the RPD of DS and CS.
The dispersion of fractal dimension, \( f(\alpha) \), is plotted as function of \( \alpha \) in Figure 9 to further analyze the RPD for DLA having different sizes. As can be seen in Figure 9, the \( f(\alpha) \) profiles show that the RPD of the DLA is characterized by a wide range of \( \alpha \) values, indicating the existence of multifractality. Like \( f(\alpha) \) in the DS case, the \( \alpha \) range shifts to lower values as DLA radii (\( L \)) increase. Differences also exist. First, the range of \( \alpha \) values in DLA is not constant: It decreases as the radii increase. This can be explained by the RPD at each position in Figure 7. As shown in Figure 7, the smaller size of DLA leads to a much higher position sensitivity than does the bigger one, namely, the sites having larger reaction probabilities are distributed in a narrower region. For larger DLA, a great number of lower reacting probability sites level out the distribution and thus lower the position distinction. Second, the \( f(\alpha) \) figures are asymmetric with respect to \( \alpha \), in contrast to the symmetric \( f(\alpha) \) profiles of CS and DS. The key feature is that the curve contracts upwardly at high \( \alpha \) value. This interesting feature comes from the unevenness of the number of lowest reacting probability sites and the number of large reacting probability sites.

VI. Conclusions

We performed DLA simulation on a two-dimensional square lattice to study the effect of a square launching boundary and nonfixed center on DLA. A square boundary is found to be superior to a circular one for its vulnerability to initiate the first few aggregation events and
Figure 8. $\tau(q)-q$ curves for different sizes of DLA. Solid, dashed and dotted lines stand for 1,000-, 3,000-, and 10,000-particle DLA clusters, respectively.

less CPU consumption. The resulting clusters have comparatively isotropic contours rather than the diamondlike ones obtained in the conventional DLA simulations using a circular particle-releasing boundary. The nonfixed seed model gives us some clues from which we can bridge the Witten–Sander DLA to the Eden model. This has been done by combining fixed-seed and nonfixed seed models in an appropriate way in the simulations. By changing the weighing ratios of these two models, we obtain a continuous change of the fractal dimensionality from the Witten–Sander limit to the Eden limit.

A generalized BRW algorithm was adopted to simulate the effect of an attractive drift on the DLA pattern. By varying the two components, $F_c$ and $F_r$, of the drift, a fruitful of cluster patterns with different morphologies can be produced. In the case of $F_c \ll F_r$, a "+"-shaped cluster is formed, indicating a pure axial anisotropy. On the other hand, i.e., $F_c \gg F_r$, an "x"-shaped cluster is generated, indicating a pure diagonal anisotropy. In between these two limiting cases, an eight-lobed cluster is formed that shows the combined anisotropic morphologies. In all cases when the $\alpha$ value becomes very small, all patterns are found to be reduced to ordinary DLA.

Multifractal analyses of the RPD were performed for a diffusion-limited reaction over the DLA surface. Analysis of the DLA size-effect indicates multifractal scaling of the distribution of the reaction probability over the DLA surface. Unlike the dispersions of fractal dimension of DS and CS, $f(\alpha)$ profiles of DLA were found to have a wider range of $\alpha$ values and asymmetric outlooks with respect to $\alpha$. This can be rationalized by noting that a large fraction of inner surface sites on a DLA were screened by the outer active sites. Similar to that for DS, the
$\alpha$ range shifts to lower value as DLA size increases. The significant difference of the $f(\alpha)$ spectrum also manifests the high sensitivity of catalysis to structure even in a basic reaction like the Eley–Ridel DLR.

Acknowledgment

The authors thank the National Science Council, Taiwan, Republic of China, for financial support.

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Received June 28, 1993
Accepted for publication January 29, 1994