Pattern Formation in Diffusion-Limited Aggregation

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The diffusion-limited-aggregation model is generalized in order to take into account the surface effects playing an essential role during most of the growth processes. With variation of a parameter of the model the geometry of the clusters generated in the Monte Carlo simulations gradually changes from the randomly branched diffusion-limited-aggregation clusters into compact, nearly regular, snowflakelike patterns. The deposition of particles along a line results in patterns similar to those observed in the experiments on directional solidification.

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Patterns formed by nonequilibrium growth processes such as aggregation[1] or dendritic-crystal growth[2] have attracted great interest recently. One of the main reasons for this interest is that the investigation of aggregates and dendritic crystals has much practical importance, since they appear in a wide range of phenomena in science and technology. Second, the theories for such nonequilibrium processes have raised a number of unsolved fundamental problems about the structure of aggregates and the mechanism by which a pattern is spontaneously selected by a growing crystal. A simple aggregation model giving direct insight into a pattern-forming process is expected to contribute to the understanding of this extensively studied phenomenon.

In the diffusion-limited-aggregation (DLA) model[3] randomly branched, sparse clusters are generated as diffusing particles stick to the surface of the growing aggregate. The density correlations decay algebraically in these clusters, i.e., there is no characteristic length within one large aggregate and it can be described by its fractal dimension.[4] Although—as it was discussed by Witten and Sander[3]—the DLA model is related to the equations describing dendritic-crystal growth, the regularity of the patterns observed in the experiments on growth of crystals in undercooled melts has not been found in DLA. In an attempt to account for the surface tension, Rikvold[5] used a finite-screening-length stochastic model for the cluster growth and obtained compact clusters but without any regular shape.

The patterns appearing during nonequilibrium crystal growth result from the competition between the nonlocal diffusion field amplifying the growth at places where the crystal bulges deeper into the undercooled liquid and the surface tension which favors flat interfaces.[6] In the theory of pattern formation during crystallization elaborated by Langer and co-workers,[7–9] the regular pattern of the crystals grown under nonequilibrium conditions has its explanation in the marginal-stability principle. This conjecture is in good agreement with the experimental results but it has not been rigorously proven yet. In numerical calculations based on theoretical models[10,11] for the interface development, some of the main features of the dendritic-crystal growth were found. Realistic patterns, however, have only been obtained in models which assume that the motion of a particular point of the interface depends merely on the local environment of that point. Models of directional solidification have also been studied both theoretically and numerically[12–14] and interface shapes similar to those observed in the related experiments[15] were obtained.

The main problem addressed in this paper is the following: What is the relationship of the above two approaches? How does a regular pattern emerge from a purely random process? In this communication a simple diffusion-limited-aggregation model is presented in which both the random and the regular behavior appears. Changing a parameter one is able to show—for the first time—how in a Monte Carlo simulation of the same model *both* low-density *fractal clusters* and compact, nearly *regular* snowflakelike *patterns* appear spontaneously. The process analogous to directional solidification can also be studied leading to a pattern with a characteristic wavelength λ. The direct simulation of the pattern-forming process allows one to draw a number of important conclusions about the nature of this phenomenon.

The model investigated in this paper is a generalization of the DLA model in which randomly walking particles launched from distant points stick to the surface of the growing cluster when they arrive at a site adjacent to the aggregate. In addition to the above process corresponding to a *nonlocal* diffusion field, in the present model two further rules are in-

troduced in order to take into account the surface effects. (i) The sticking probability of the particles arriving at the surface of the aggregate is assumed to depend on the *local* curvature of the surface. If the particle does not stick to the surface it continues diffusing; thus the growth rate is reduced at places with large interface curvature. (ii) After a particle has been allowed to land, its position is relaxed to one of the nearest- or next-nearest-neighbor sites with the lowest potential energy (with the largest number of occupied nearest neighbors).

The above model combines two methods: first, a direct simulation of the diffusion motion of individual aggregating particles and second, a Monte Carlo approach to the solution of the continuum equations for the solidification problem. Correspondingly, the sticking probability rule is an approximation to a form of the Gibbs-Thomson relation which is used as a boundary condition in the continuum models. On the other hand, surface relaxation (rule ii) simulates a microscopic process, namely, the dynamic reshuffling of molecules at nonfaceted solidification interfaces. Without surface relaxation, randomly ramified structures are generated, with many holes and an approximately constant density $\rho \approx 0.6$. Going to nearest-, next-nearest, and third-nearest-neighbor relaxation results in a smoother interface and disappearance of holes, giving in the latter case almost perfectly compact clusters.

The actual simulations were carried out on square lattices. In the directional-growth case, 400^2 cells were used with periodic boundary conditions. The local curvature of the interface at a lattice site r was characterized by the number of particles N_l belonging to the aggregate and being within a cell of size $l \times l$ centered at point r. Obviously, the case $n_l = N_l/l^2 << 1$ (where n_l is the normalized value of N_l) corresponds to a large positive curvature, while for $n_l \simeq 1$ the local geometry can be interpreted as corresponding to a large negative curvature. For the dependence of the sticking probability $p(n_l)$ on the curvature, the simplest choice was made; it was assumed that $p(n_l)$ depended on n_l linearly, namely

$$p(n_l) = A(n_l - n_0) + B, \tag{1}$$

where $n_0 = (l-1)/2l$ corresponds to a flat interface touching the point r at which the particle contacts the surface. Of course, if (1) gave $p(n_l) > 1$ I assumed that $p(n_l) = 1$. For the case when the sticking probability obtained from (1) was less than a small constant $C = 0.01$, the value $p(n_l) = C$ was used to keep the growth process going on even for small n_l, thus saving computer time. However, the parameter C does not play any significant role and it is enough to change either A or B to see crossover in the behavior of the system. The size of the cell, l, at the surface in which the number of particles belonging to the cluster N_l was counted was equal to 9 or 11 in most of the cases. For a fixed curvature (fixed n_l), the sticking probability increases linearly with A just as the local melting temperature in the Gibbs-Thomson condition changes linearly with the surface tension γ. In this respect A and $-\gamma$ are analogous; however, the direct calculation of a measurable γ would require more details specified in the present model. The expression (1) for $p(n_l)$ is not expected to satisfy detailed balance, since the microscopic events (sticking to the cluster) are not reversible in this model.

Figure 1 shows the growth of a cluster starting from a single seed particle. The choice $A = 5.0$, $B = 0.5$, and $l = 9$ results in a cluster which is very much different from the diffusion-limited aggregates and shares some features with the ice crystals formed in glacier cavities.[16] Because of the surface-curvature-dependent sticking probability, the random branches typical for a DLA cluster do not appear. Recently it has been shown[10,11,17] that an-

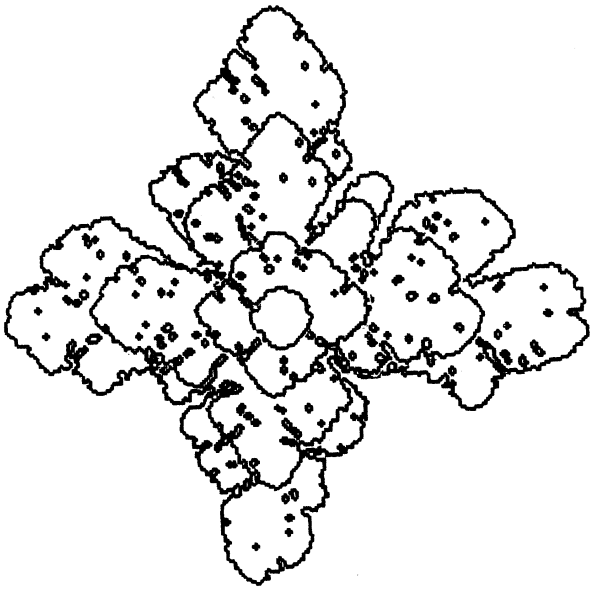

FIG. 1. Typical cluster of $M = 24\,000$ particles grown from a seed particle. Only the surface sites (those which have less than four occupied nearest neighbors) are plotted. The parameters in the expression for the curvature-dependent sticking probability were $A = 5.0$ and $B = 0.5$. The earlier stages of the growth process at $M = 500$, $M = 3000$, and $M = 12\,000$ are also shown.

isotropy plays a crucial role in the formation of patterns in dendritic solidification. The fourfold snowflake shown in Fig. 1 is a result of the anisotropy imposed in this model by the square lattice, since the condition (1) for $p(n_l)$ does not depend on the local orientation of the interface. This kind of anisotropy is generated by a simple mechanism: When growing a nearly circular object on a square lattice layer by layer [at early stages this process is preferred by Eq. (1)], one inevitably arrives at an approximately square shape. Then the straight edges of this square become unstable against perturbations having curvature comparable to the tip radius of the corners (see next paragraph). However, it is simple to introduce an explicit anisotropy into the model by definition of an orientation dependent $p(n_l)$ which corresponds to an anisotropic surface tension used in the continuum models.[10,11,17] The clusters obtained with an increased sticking probability along the axes or the diagonals of the square lattice have sharper tips and more regular shape. In Fig. 1 the different stages of the growth process are identified by the number of particles in the cluster, which is not the same as keeping track of the physical time. A possible way to introduce direct time dependence (and to measure the tip velocity of the dendrites) is to start the process with many particles diffusing simultaneously and sticking to the surface of the growing aggregate placed at the origin.

The role of anisotropy is expected to be less important in the series of Monte Carlo experiments on the deposition process[18,19] along a line of length L. In Fig. 2 clusters made of diffusing particles deposited on a line are shown. To demonstrate how the change in the value of the parameter A leads from a random DLA-type deposit to a nearly regular pattern, results of runs with various A are displayed. It can be easily seen that as A is increased (this corresponds to a stronger effect of the surface curvature), the interface becomes more regular and a quasiperiodic structure is built up. For times that are not too long, this interface can be described in terms of a characteristic wavelength which is selected by the interplay of the fluctuations: the long-wavelength destabilizing force of the diffusion field and the local stabilizing mechanism of the curvature-dependent sticking probability. A possible way of estimating this wavelength is to calculate the integral $I(\omega)=\int_0^L \sin(2\pi\omega x)m(x)dx$, where $m(x)$ is the envelope of the surface [x is the distance along the deposit and $m(x)$ denotes the coordinate of the most advanced point at x belonging to the surface]. The typical wavelength $\lambda(A)$ appears as a distinct

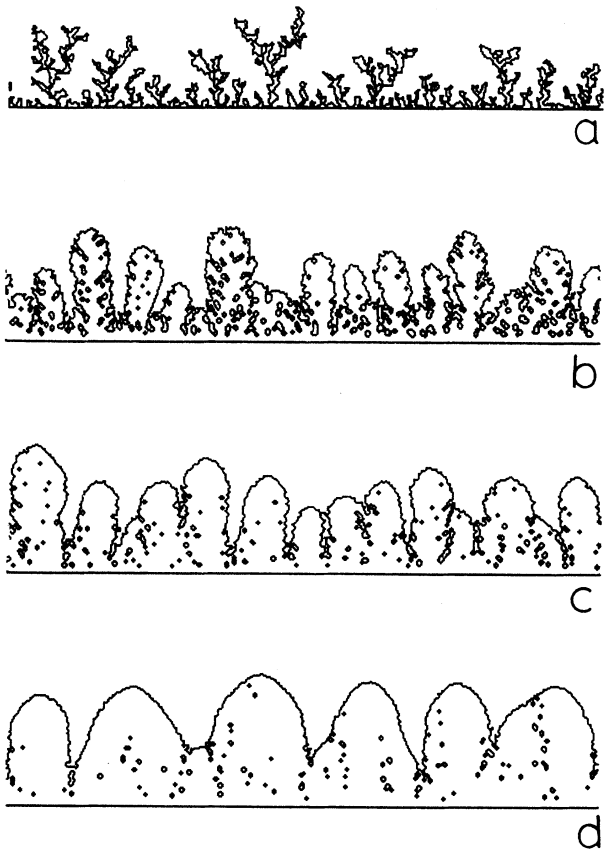

FIG. 2. Interface of the deposits for various values of the parameter A. The following values were used (in all cases $l=11$): (a) $A=0.0$, $B=1.0$; (b) $A=3.0$, $B=0.5$; (c) $A=6.0$, $B=0.5$; and (d) $A=12.0$, $B=0.5$. As the role of the surface curvature is increased [(a) corresponds to zero surface tension] the randomness of the interface becomes less significant and a nearly regular pattern develops with a characteristic wavelength increasing with A.

peak at $\omega(A)$ in $I(\omega)$. [There are, of course, some more trivial peaks in $I(\omega)$ as a result of the finiteness of the interval on which this Fourier-type analysis is made.] In Fig. 3 the dependence of $\lambda(A)$ on the parameter A is shown.

With increasing number of deposited particles, the structures shown in Figs. 2(b)–2(d) become unstable and a configuration analogous to Fig. 2(a) develops. In the limit of large A, a well defined crossover can be observed from the cellular to a random pattern. However, it is possible to obtain linearly stable patterns in this model by introducing biased diffusion. By increasing the probability of jumping downward, one can simulate the effects of a thermal gradient imposed onto the system in directional-solidification experiments. In this way,

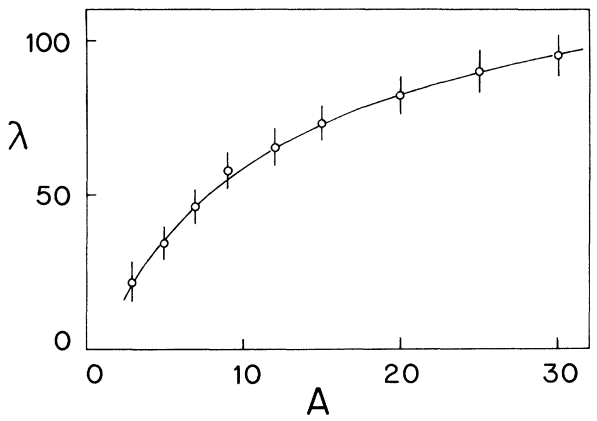

FIG. 3. Dependence of the characteristic wavelength in the deposits on the parameter A for fixed $B = 0.5$.

stable cellular patterns can be generated in good agreement with the experimental observations.[15]

Although most of the results presented in this paper are more qualitative than quantitative, one can draw a number of important conclusions about the nature of the mechanism which leads to pattern formation in diffusion-controlled systems. (i) Surface tension (simulated by the curvature-dependent sticking probability) and the anisotropy (provided by the square lattice) produce nearly regular patterns in diffusion-limited aggregation. (ii) For the curvature-independent case, all wavelengths are equally present. With the increasing dependence on the interface curvature, however, the tips of the growing dendrites become rounded. As a result more particles are involved in the growth of one dendrite and the fluctuations become relatively less important. Consequently, at least at the beginning, the growth rate of the tips is less different and a more regular pattern is obtained. It is expected, however, that in the deposition model after a long time, a crossover from a cellular to a dendritic structure takes place, while the characteristic radius of the tips remains constant. (iii) The fact that the dendrite tips have approximately the same radius (although other tip radii would also be stable) is in accord with the theories about pattern selection.[2] (iv) The rule of relaxing the particle to a neighboring position with the smallest potential energy plays an important role in getting compact clusters. Without this rule, ramified clusters are obtained showing that surface migration during growth processes with surface tension is essential.

Finally, the model introduced in this paper can be relatively easily modified in order to take into account some more factors such as anisotropy or external field which effect pattern formation. In this way the relevance of these details during nonequilibrium growth processes can also be investigated. Application of the model to the off-lattice or to the three-dimensional case is straightforward and is expected to provide important new information.

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