Formation of solidification patterns in aggregation models

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(Received 4 April 1985)

Generalizations of the diffusion-limited aggregation model are considered in order to simulate pattern formation during solidification. The two-dimensional clusters grown on a seed particle are initially circular but at later stages the process crosses over into dendritic growth. The effects of an anisotropic surface tension are studied by assuming that the sticking probability of the particles depends on the local orientation of the interface. Directional solidification is simulated by the deposition of particles undergoing biased random walks. Linearly stable patterns are generated if the basic features of the directional solidification experiments are taken into account. The resulting patterns are very similar to those observed experimentally.

I. INTRODUCTION

The formation of patterns by growing interfaces is one of the main processes in a wide range of phenomena in science and technology. Such behavior is exhibited during solidification, when the crystalline phase is growing in supersaturated vapor or undercooled melt.[1] Examples of formation of solidification patterns include the evolution of a snowflake in the atmosphere or directional solidification in a number of metallurgically important situations.[2]

During crystal growth in an undercooled melt the temperature gradient acts as a nonlocal destabilizing force which amplifies the growth at places where the crystal bulges into the cooler regions of the liquid phase. On the other hand, the surface tension, which is related to the local surface energy, favors minimum surface area, or in other words, flat interfaces. The patterns emerging from the originally homogeneous phase are results of the competition of these forces.[3] The process of solidification is described by nonlinear partial-differential equations and both the analytical and the numerical treatments of these equations are extremely difficult. As a result, many of the questions concerning pattern formation have not so far been satisfactorily answered. The marginal stability hypothesis[4–6] provides a rule for the selection of a particular tip shape through the parameters of the problem; however it has not been proved yet. One possible way to examine the above questions is through the study of model systems which produce patterns.[7–10]

Several simplified models have been introduced recently in order to make the originally very complex mathematical problem tractable. One class of these models is based on the assumption that the motion of the surface is merely determined by local properties. In the boundary-layer model of Ben-Jacob *et al.*[8] the characteristic decay length of the diffusion field is assumed to be much smaller than the local radius of curvature of the interface. The local-evolution model of Brower *et al.*[9] is based on the purely geometrical aspects of moving boundaries. Some of the results obtained from this approach[11] are not in accordance with the marginal stability hypothesis. Although the local models have succeeded in explaining a number of important features of dendritic growth they do not take fully into account the nonlocal character of the diffusion field surrounding the growing crystal and effecting the solidification process. Consequently, in many cases they lead to nonphysical results (overlap of the dendrites) for long times.

To simulate the behavior of the solidification front in the presence of nonlocal driving forces one needs new numerical methods and models. The diffusion-limited aggregation (DLA) model[12] of Witten and Sander seems to be particularly appropriate for treating the effects of the nonlocal diffusion field. In the Monte Carlo simulations of this model, randomly branched, fractal[13] clusters are generated as diffusing particles launched from distant points stick to the surface of the growing cluster when they arrive at a site adjacent to the aggregate. In its original form, however, DLA did not produce regular dendritelike patterns, because the surface effects were not taken into account in a way consistent with the differential-equation approach. In a recent paper (Ref. 7) a simple generalization of the diffusion-limited aggregation model was introduced in which the stabilizing force of the surface tension was accounted for through a local-curvature-dependent sticking probability. The simulations of this model produced nearly regular patterns showing that this generalized DLA process is suitable for studying the formation of solidification patterns. Very recently Kadanoff[14] proposed another generalization of the diffusion-limited aggregation model in order to simulate pattern formation in hydrodynamics.[15,16] A more traditional method, namely, the numerical solution of the original differential equations, has also been explored recently by Kessler *et al.*[10] who applied the contour-dynamics method to the two-dimensional dendritic crystal growth.

In this paper the aggregation approach (Sec. II) is used to generate solidification patterns. In Sec. III results are presented for dendritic growth with an anisotropic surface tension. Directional solidification is studied in Sec. IV. The conclusions are given in Sec. V.

II. MODEL

The motion of the solidification front is determined by the diffusion field at the point x at time t, $u(x,t)$, which

satisfies the equation

$$\Delta u(x,t)=0 \tag{1}$$

if we assume that the interface moves slowly. As it was discussed by Witten and Sander[12] and by Kadanoff[14] the probability that a randomly walking particle released far from the surface is at the point x at time t obeys the discrete version of Eq. (1). Therefore, the diffusion-limited aggregation models are potentially good candidates for obtaining solidification patterns. Equation (1), however, should be solved by taking into account that the interface temperature $T_{\rm int}$ is related to the melting temperature T_M through the following form of the Gibbs-Thomson relation[17]

$$T_{\rm int}=T_M(1-\gamma K/H)\ , \tag{2}$$

where γ is the surface tension, K is the local curvature of the interface, and H is the latent heat. (The other boundary condition, heat conservation at the interface, is not expected to play an important role from the point of view of our approach.)

To simulate the effects of the Gibbs-Thomson condition we modify the original DLA model and assume that the probability of sticking to the surface of the aggregate depends on the local curvature of the interface.[7] According to the boundary condition (2), if $K>0$ (the surface bulges into the undercooled liquid), $T_{\rm int}$ becomes smaller than T_M and the local temperature gradient will be decreased. This effect slows down the local growth rate. In order to account for this stabilizing property of the surface tension we define a sticking probability which is smaller at the places where $K>0$ and as a result we expect the aggregate to grow slower at these sites (a particle which does not stick to the surface diffuses away).

As the measure of the local surface curvature at the point x in the two-dimensional simulations one can use the number of particles (N_L) which belong to the aggregate and are within a cell of size $L\times L$ centered at point x. Assuming that the characteristic changes in the shape of the surface take place on a larger scale than L, the quantity n_L-n_0 can be regarded as a rough estimate of the average local curvature. Here $n_L=N_L/L^2$ and $n_0=(L-1)/2L$, where n_0 corresponds to a flat interface touching the point x at which the particle contacts the surface. Therefore, our rule for the sticking probability is local only in the sense that it depends on an average local curvature (just as the surface temperature in the continuum models), but it is not completely local because not only the nearest neighbors in the aggregate are supposed to affect the growth at a given site. This is in the spirit of the Gibbs-Thomson condition: it considers an interface with a well-defined curvature, although real nonfaceted crystal interfaces are rough at the molecular level and are smoothly rounded only on a macroscopic scale. Another way of determining the local surface curvature by directly calculating the second derivative of the interface at the point x was recently proposed by Kadanoff.[14] We use n_L for estimating K because this approach is simpler and provides reasonable estimates as well.

Next we need an expression for the dependence of the sticking probability $p(n)$ on the curvature K, which is represented in our approach by the normalized number of particles n within the box surrounding the place of arrival at the interface. One of the simplest choices is

$$p(n)=A(n-n_0)+B\ , \tag{3}$$

where A and B are constants. It is possible to establish a connection between our approach and the Gibbs-Thomson relation by writing (3) in the form $p(n)=B[1-A/B(n_0-n)]$, which is the same as (2) with $B=T_M$, $A/B=\gamma/H$, and $n_0-n=K$. In the simulations, if (3) gives $p(n)>1$, then $p(n)=1$ is used. For the case when the sticking probability given by (3) is less than a small constant $C=0.01$, the value $p(n)=C$ is used to keep the growth process going on even for small n, 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 from the random-fractal into the snowflake-growth regime.

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. In this way every time a particle touched the surface, 81 or 121 sites were checked in order to get information about the local surface curvature. In the stochastic model of Rikvold[18] the occupation probability of a given site was directly proportional to the number of occupied nearest neighbors of that site. This, however, turned out to be not enough to simulate the main effects caused by the surface, and the compact, irregular clusters he obtained were results of the finite screening length used in that model.

A simulation using condition (2) for the sticking probability in general leads to nonfractal clusters in the sense that the particle density inside the hull of the clusters is approximately constant. The surface of these clusters, however, is still quite ramified and they also contain a considerable number of defects resulting in an average density which is definitely less than one. Therefore, an additional rule was used to obtain clusters which have a well-defined surface and a density close to one.[7] This goal can be achieved by the following process. After a particle has been allowed to land it is relaxed to one of its neighbor sites. The new position is chosen in such a way that it has the highest number of occupied nearest neighbors (lowest potential energy). This process simulates a microscopic phenomenon, namely, the dynamic reshuffling of molecules at nonfaceted solidification interfaces.

In summary, the rules of the model are the following:

(i) Random walks by the particles (as in DLA),

(ii) Sticking to the surface of the growing cluster with a probability depending on the local interface curvature,

(iii) Relaxation to a position with the highest number of occupied nearest neighbors.

Application of the above model to the solidification problem has a number of advantages. The numerical method is simple and effective, and relatively complex geometries can be generated easily. Second, the fluctuations which are always present in a thermodynamical system (and play an important role during the growth process) are included in a natural way through the random walks of the particles. Finally, the model can easily be

modified in order to take into account various experimental conditions. For example, the effects of an anisotropic surface tension or a temperature gradient imposed upon the system can be directly simulated.

III. DENDRITIC GROWTH

In order to simulate dendritic growth the model described in Sec. II was used with a single seed particle on a square lattice. The process starts with a growing, nearly circular cluster since at this stage the surface-area-minimizing effect of the curvature-dependent sticking probability dominates the growth. Above a certain characteristic radius r_c (depending on the parameter A, a quantity analogous to the surface tension), however, this circular shape becomes similar to a square with rounded corners. This effect is caused by the underlying lattice. The cluster prefers to grow layer by layer and on a square lattice this process inevitably results in a biased, square-like pattern. At later stages of the growth process the corners of this square ("bulging" into the "undercooled" region) become unstable and start growing faster than the straight edges of the cluster. On these growing dendrites new unstable regions appear and become dendrites themselves as well. In general, large values of A result in more symmetric patterns, larger r_c (smaller curvatures), and a smooth surface.

In order to demonstrate how the initially structureless behavior crosses over into dendritic growth in Fig. 1 we show the number of surface sites N_s versus the number of sites in the cluster N in a log-log plot. For relatively small sizes the slope of the straight line connecting the data is approximately equal to $\frac{1}{2}$ in accordance with the growth of a circular cluster. At later stages, however, the number of surface sites becomes linearly proportional to N (resulting in a slope nearly equal to 1) which corresponds to the development of dendrites.

At the further stages of the growth process, however, another crossover is likely to occur. Since the rule is essentially local, as the size of a cluster increases, its structure is expected to approach the random-fractal geometry of a diffusion-limited aggregate. On the other hand this crossover to the fractal structure takes place on a length scale which is outside of the region studied in the present work.

As was discussed in the first paragraph of this section, the symmetry properties of the lattice on which the growth process takes place have an effect on the shape of the resulting cluster. This fact, however, is not the only way through which anisotropy can influence the results. The role of an anisotropic surface tension has been the subject of recent publications.[10,19,20] It has been shown that also in the local-evolution approach stable dendritic growth could be observed only if the anisotropy of the surface tension exceeded a critical value.[20] In addition, the numerical integration of the solidification equations led to the same conclusion.[10]

The effect of an anisotropic surface tension can be investigated in the present model by introducing a sticking probability p_{an} depending on the local slope of the surface. If we are interested only in the qualitative conse-

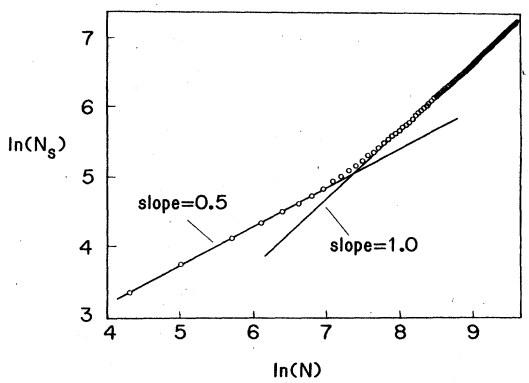

FIG. 1. Dependence of the number of surface sites N_s on the number of particles in the cluster N. The change in the slope of the curve indicates the crossover from compact to dendritic growth.

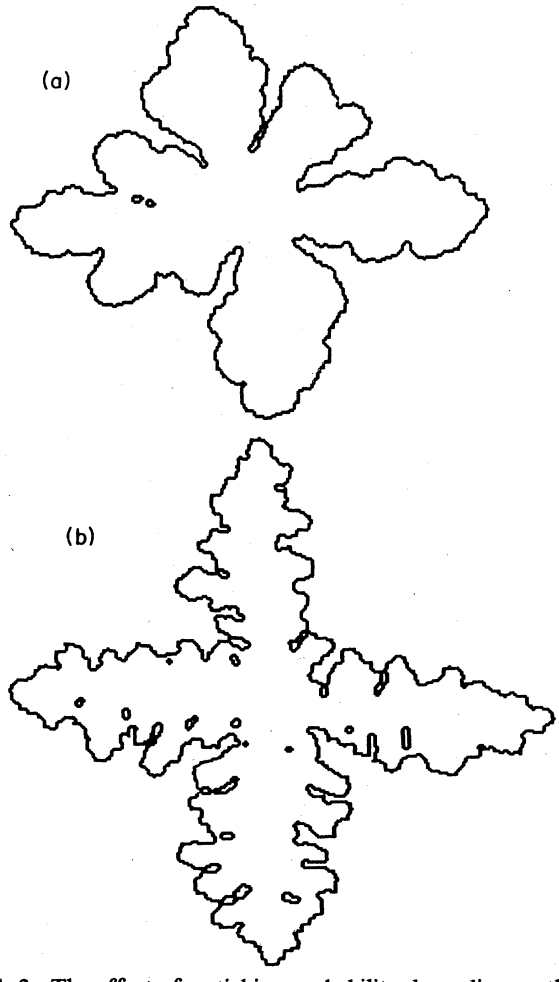

FIG. 2. The effect of a sticking probability depending on the local orientation of the surface. In (a) a cluster of 21 000 particles is shown with no anisotropy of the surface tension (sticking probability). Only the surface sites (those which have less than four occupied nearest neighbors) are plotted. (b) shows a cluster of 25 000 particles generated using a condition for the sticking probability which enhances growth along the axes of the square lattice.

quences of the anisotropy, we can use a construction similar to that which was used for estimating the curvature. Again, the square cell of size $L \times L$ is considered, and the number of occupied sites (normalized by L) along its left, right, top, and bottom edges, n_l, n_r, n_t, and n_b, respectively, is counted. It is easy to see that the quantity $S = |n_l - n_r| + |n_t - n_b|$ is related to the local slope. If $S \simeq 1$, the vector normal to the surface at point x is approximately directed along one of the main axes of the square lattice, while for $S \simeq 2$ it is directed along one of the diagonals. Therefore, we can use for the slope-dependent sticking probability the expression $p_{an}(n) = p(n) p_{an}$ with $p_{an} = [1 - D(S-1)]^a$, where D and a are parameters. For $D > 0$ and $a > 0$ this expression provides an enhanced growth along the main axes of the square lattice.

In Fig. 2(a) a cluster of 21 000 particles is shown. This pattern was obtained using the parameter values $A = 4.0$, $B = 0.5$, and $D = 0$ and allowing a third-nearest-neighbor relaxation. Although the geometry of the cluster reflects the symmetry of the underlying lattice, this feature is not pronounced and something like a tip splitting of one of the dendrites can also be observed which is due to the lack of the anisotropic surface tension. The overall appearance of this cluster is similar to the ice crystals which can be found in glacier cavities.[21] The splitting of the dendrite tips is a more common phenomenon for the clusters which are grown using smaller values of A. There seems to exist a critical value for the surface-tension-like parameter A for which the anisotropy of the lattice itself provides stable dendritic growth.

In Fig. 2(b) a cluster of 25 000 particles is shown which was generated for $A = 3.25$, $B = 0.5$, $L = 4$, $D = 0.125$, and $a = 2$. This pattern exhibits a number of properties typical of dendritic solidification. The four main dendrites develop side branches and the growth process appears to be stable in the sense of the absence of any tip splitting. However, this cluster is still not as regular as most of the solidification patterns observed in the experiments.[22,23] This is due to the fluctuations which are relatively large for small surface tension. For larger values of A more regular patterns are expected to grow in this model. On the other hand, we had to keep A relatively low in order to have larger curvatures and more complex patterns in our medium-scale simulations.

IV. DIRECTIONAL SOLIDIFICATION

In this section we consider a version of the model in which the particles are deposited onto a line[24–26] instead of a single particle in order to simulate the conditions of directional solidification experiments.[27,28] During these experiments the working material (usually a long rod or a thin strip) is drawn with a given velocity through a fixed temperature gradient. The sample is molten at the hotter edge of the system and frozen at the opposite side, so that the solid-liquid interface appears in between. The temperature throughout the region is changing approximately linearly with the distance z measured from one of the edges of the experimental cell. These experiments result in linearly stable, cellular solidification patterns in accordance with the theoretical results.[29–31]

As was discussed in Ref. 7, if the rules described in Sec. II are applied to the case of the deposition along a line, quasicellular patterns emerge from the simulations. The very early stages of the process can be related[32] to the Saffmann-Taylor instability.[15] The dependence of the characteristic wavelength of the patterns on A has been shown[32] to be consistent with the predictions of a linear-stability analysis of the flat interface.[15] This correspondence, however, breaks down at the later stages of the growth process and the nearly cellular pattern crosses over into a dendritic structure as demonstrated in Fig. 3. Therefore, the originally quasiperiodic interface is not stable.

The temperature gradient imposed onto the system in the directional solidification experiment results in a permanent flow of heat from the hotter to the cooler part of the system. In addition, the frame of reference is moved with a given velocity in the z direction, and Eq. (1) for this case takes the form

$$\Delta u + (2/\Lambda)(\partial u/\partial z) = 0 , \tag{4}$$

where Λ is the diffusion length. In order to account for the second term in (4) we introduce a biased random walk by increasing the probability of jumping in the direction of the interface or "downward," p_{down}, with respect to the probability of jumping "upward," p_{up}. The simulations for several values of the ratio $R = p_{down}/p_{up}$ result in patterns which are more regular for $R > 1$ than for the unbiased case. In fact, these patterns look very similar to those observed in the experiments of Heslot and Libchaber[28] on directional solidification of thin samples of succinonitrole. This is demonstrated in Fig. 4, where both the simulation and the experimental results are shown.

A more careful study of the aggregation process with a bias on the random walks shows, however, that $R > 0$ itself is not enough to account for all the effects caused by the temperature gradient and the moving of the working material. Although the growth of the fingers seems to be much more stable for $R > 0$ than for the nonbiased case, it is still expected that after a long time the solidification front becomes less regular and some of the fingers start

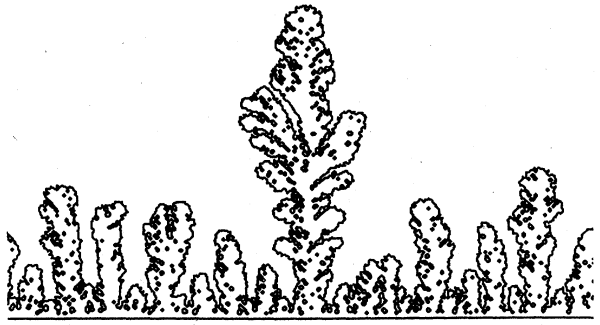

FIG. 3. This figure shows a pattern which was obtained by deposition of 45 000 particles on a line of 500 seed particles and using $A = 3.0$ and $B = 0.5$. Although at the earlier stages of the simulation a cellularlike pattern can be observed (Ref. 7), for a greater number of particles the process crosses over into dendritic growth.

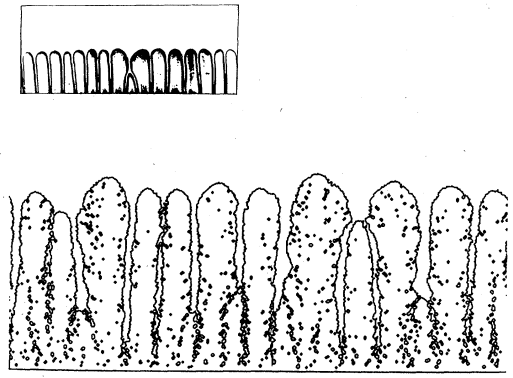

FIG. 4. This pattern was generated using $A=6.0$ and $B=0.5$ in the expression (3) and biased random walks with a ratio of downward to upward jumps of $R=1.1$. The insert shows the experimental results of Heslot and Libchaber (Ref. 28) on the directional solidification of succinonitrole.

growing faster than the neighboring ones. The picture then probably changes into a pattern analogous to the interface shown in Fig. 3. This is indicated by the fact that the envelope of the solidification front in Fig. 4 is wavy.

The reason for this phenomenon is that we have not yet taken into account that there is a relatively sharp region in the system where the temperature changes from $T<T_M$ to $T>T_M$ and that the solidification front develops in this region. It is, however, possible to simulate this feature of the directional solidification experiment as well. We achieve this goal by assuming that the sticking probability of the particles depends on the position of the surface on the lattice changing linearly with z, where z is the distance from the line on which the particles are deposited. Correspondingly, we define a z-dependent sticking probability $p_z(n)$ assuming that

$$p_z(n)=p(n)+E(z_t-z)\ , \tag{5}$$

where z_t is the z coordinate of the most advanced part of the solidification front and E is a parameter used to simulate the effects of the temperature gradient. The condition (5) for $E>0$ leads to an aggregation process in which the most advanced fingers grow somewhat slower (being in a "warmer" environment), while the others (having a higher sticking probability for those z values) have a better chance to advance. As a result, the envelope of the solidification front is more balanced and a linearly stable pattern develops during the simulation in accordance with the theoretical and experimental results. A pattern generated using biased walks and the expressions (3) and (5) for the sticking probability is presented in Fig. 5. The values of the parameters in this simulation were $A=3.5$, $B=0.2$, $E=0.02$, and $R=1.05$. The tips of the fingers are situated approximately at the same level just as observed in the experiments.

V. CONCLUSIONS

Several generalizations of the diffusion-limited aggregation model have been applied to the problem of pattern formation during solidification. It has been shown that

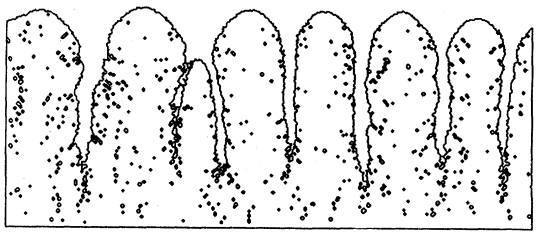

FIG. 5. The interface of a deposit which was obtained using the expressions (3) and (5) with $A=3.5$, $B=0.2$, and $E=0.02$ for the sticking probability and biased random walks with $R=1.05$. This is the most complete simulation of the directional solidification, with a linearly stable solidification front.

the aggregation model proposed in Ref. 7 produces patterns which have properties consistent with the experimental observations. These patterns emerge from an entirely random process which leads to either fractal objects or to nearly regular solidification patterns depending on the value of the parameter A corresponding to the surface tension.

Studies of the growth process started from a seed particle show a crossover from compact to dendritic growth which can be demonstrated by plotting the number of surface sites versus the number of particles in the clusters. The introduction of a sticking probability depending on the local orientation of the surface results in more stable growth and relatively well-defined side branches appearing on the main dendrites. There seems to exist a critical value for the parameter A beyond which the anisotropy of the underlying lattice becomes the source of stable dendritic growth.

Two-dimensional directional solidification can be simulated by the process of deposition on a line. The patterns obtained from the simulations are linearly stable and very similar to the pictures observed in the experiments on succinonitrole. The characteristic wavelength of the solidification front can be controlled by both the surface-tension-like parameter A and the parameters E and R corresponding to the temperature gradient imposed onto the experimental system.

The cluster shapes generated in the simulations reported in this paper are less regular than most of the solidification patterns which can be found in nature or obtained in the related experiments. There are indications that the role of elementary fluctuations of size comparable to the lattice constant is decreased if the simulations are made using parameter values corresponding to a larger surface tension (smaller curvatures). In this case, however, many more particles should be incorporated into a cluster in order to get relatively complex patterns. Work along this line is in progress.

ACKNOWLEDGMENTS

The author thanks F. Family, L. P. Kadanoff, L. Libchaber, B. Shraiman, and Z. Racz for useful discussions and S. Sarkar for communicating his results prior to publication. This research was supported by the Research Corporation, the Emory University Research Fund, and the National Science Foundation under Grant No. DMR-82-08051.

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