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Continuum approach to diffusion-limited-aggregation type of growth

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Models of kinetic growth phenomena analogous to diffusion-limited aggregation are introduced. The presence of two coupled fields enables the removal of nonlocality in the growth equations. Simple modifications of the model lead to a range of patterns similar to those observed in recent electrochemical deposition experiments.

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Growing structures such as diffusion-limited aggregation (DLA), viscous fingering, solidification, dielectric breakdown, and electrodeposition may all be understood in terms of a common framework involving the solution of Laplace's equation with suitable boundary conditions [1–10]. The growth process in DLA is nonlocal and involves the screening of the interior of the cluster leading to tenuous fractal structures. The conventional approaches for the simulation of such processes has involved variants of one of the following: (i) discrete DLA growth models where a particle walks randomly until it touches the cluster and then gets attached, (ii) a direct numerical solution of Laplace's equation (a steady state limit of the diffusion equation) with appropriate boundary conditions *on* the growing interface—the growth is taken to be proportional to the gradient of the Laplacian field at the interface (in the simplest version). The second method allows one to treat the problem in the continuum limit and to model nonlocal fractal growth dynamics [11]. It has two technical disadvantages—first the solution of Laplace's equation is time-consuming, being a nonlocal problem, and second, the growing interface needs to be identified and kept track of accurately, since the boundary condition is specified at this interface.

In this paper, we introduce simple stochastic differential equations for the study of a large class of problems including DLA. The nonlocality is removed by the introduction of two coupled fields, f and g, f describing the presence ($f > 0$) or absence ($f < 0$) of the aggregate and g describing the field causing the growth. Further, the need for continuous identification of the interface is avoided—no boundary conditions are imposed at the interface ($f = 0$). In the Laplacian growth limit (the cluster growth rate is small) our numerical results are in quantitative accord with previous work [2]. Another class of behavior is obtained for large cluster growth rates—the diffusion equation can then no longer be approximated by Laplace's equation. Patterns distinct from the DLA ones and similar to those obtained by Kahanda *et al.* in electrochemical deposition [9] are produced on modifying the aggregation mechanism to allow for growth proportional to the magnitude of g at the interface rather than its gradient.

Our model is described by the equations

$$\frac{\partial f(\mathbf{r},t)}{\partial t} = \nabla^2 \frac{\partial F}{\partial f(\mathbf{r},t)} + \alpha I(\mathbf{r},t), \tag{1}$$

$$\frac{\partial g(\mathbf{r},t)}{\partial t} = D\nabla^2 g(\mathbf{r},t) - I(\mathbf{r},t), \tag{2}$$

$$F = \int \left(-\frac{1}{2} f^2 + \frac{f^4}{4} + a(\nabla f)^2 \right) dv, \tag{3}$$

where the coefficients $-\frac{1}{2}$ and $\frac{1}{4}$ in (3) set the equilibrium values of f to be ± 1. The interaction term $I > 0$ leads to a growth of f and a decay of g such that the quantity $(f + \alpha g)$ does not change with time, except for sources of the g field at the boundary. Two choices of I [12] that we have used are

$$I_1 = -\nabla f \cdot D\nabla g[\eta(\mathbf{r},t)], \tag{4}$$

$$I_2 = g|\nabla f|^2 D_2[\eta(\mathbf{r},t)]. \tag{5}$$

$\eta(\mathbf{r},t)$ is a Gaussian noise uncorrelated in space and time with mean value $V > 0$ and width W. For a planar geometry, periodic boundary conditions in the transverse direction are utilized for both the f and g fields. In the z direction, normal to the initially planar interface located at $z = 0$, f satisfies antiperiodic boundary conditions. g was held fixed at g_0 at the boundary where $f < 0$ ($z = z_u$). Alternately, in most of our runs, we varied the value of g at the boundary to maintain a constant flux $-D\nabla g$. Initially, the g field was chosen to be $g(z) = g_0 z/z_u$, whereas the f field was chosen to be the steady state solution of (1) with the I term being absent. We also studied the case of a circular geometry with analogous boundary and initial conditions except that all the runs had a fixed g at the circular boundary.

Equations (1) and (2) without the I term have a simple interpretation. Equation (1) is the standard model B dynamics [13] that conserves the total magnetization. The choice of a negative coefficient of f^2 in the expression for the free energy (3) corresponds to a temperature lower than T_c—there are two values of f that minimize the free energy; with suitable choice of the scales of x and f, these may be fixed at the values $+1$ or -1. The coefficient a in (3) is a measure of the surface tension. Equation (2) in the absence of the I term is the diffusion equation. The interface is simply defined by the $f = 0$ contour. Note that interfaces of arbitrary topologies (overhangs, handles) are allowed which is an advantage over standard approaches which focus on obtaining an evolution equation for a surface in the Monge representation.

The I term in (1) and (2) represents the aggregation rate of g particles in the $f = +1$ phase. I_1 in (4) arises from the following considerations: $-D\nabla g$ is the flux of g particles while ∇f is a vector normal to the constant f surfaces (∇f is substantially different from zero only near the interface). The same I term with opposite sign in (2) takes into account the removal of the g field at the aggregate. In both (4) and (5), V is the average aggregation rate whereas W is a measure of the fluctuations in the growth rate. From the central limit theorem, $W \sim |\nabla g|^{-1/2}$ in (4) although our simulations show that the large scale properties of the aggregate are unaffected by the specific value of W. The I_2 term in (5) provides a growth mechanism proportional to the value of g itself. Unlike the I_1 case, the value of g is nonzero at the interface and allows for a flux of g with a nonzero component in a direction parallel to the interface.

Our approach is a variant of methods previously proposed in two different contexts: the phase field model [14] introduces two coupled differential equations for describing solidification, one for the temperature and the other for the phase field—no distinction is made between the solid and the liquid phases during the numerical integration [15]. In a context somewhat more similar to the present work, several workers [16] have studied coupled differential equations to monitor the dynamics of growth processes. In all aggregation models, the sum of the diffusive and aggregating fields (f and g) is conserved. While the phase field model incorporates a surface tension naturally, the interaction mechanism is such that both solidification and melting at the solid-fluid interface are permitted. In our model, the g-f conversion is unidirectional—the f field grows at the expense of the g field. Further, the interaction mechanism is decoupled from the surface diffusion—the choice of conserved order parameter dynamics for the deterministic part of Eq. (1) is a natural physics requirement, since the aggregate particles can only be redistributed locally via surface diffusion. Further, a conservation law is operative even far from the interface. The nonconserved coupling part is responsible for the growth of the interface.

Our approach is to define two fields, one of the diffusing particles and the other characterizing the growing aggregate. The basic idea is that due to the interaction of the two fields, the diffusing particles join the growing aggregate at its surface leading to the conversion of one field into the other. In the phase field method, the solid phase itself is characterized by nonconserved dynamics—i.e., the analog of our f field does not have a conservation law.

We have carried out detailed numerical studies of the model in two dimensions in both planar and circular geometries. The coefficient α in (1) has been set equal to 1 in our simulations. Equations (1)–(5) were solved on a discrete square grid with lattice constant equal to 1, and the integration time step equal to 0.01. Control runs were performed with half the time step to ensure that the results were statistically the same. For computational ease, the interaction term was assumed to be operational only when $|f| < 0.8$—the remnants of the g field ($< 2\%$) were converted to f in the region $f > 0.8$.

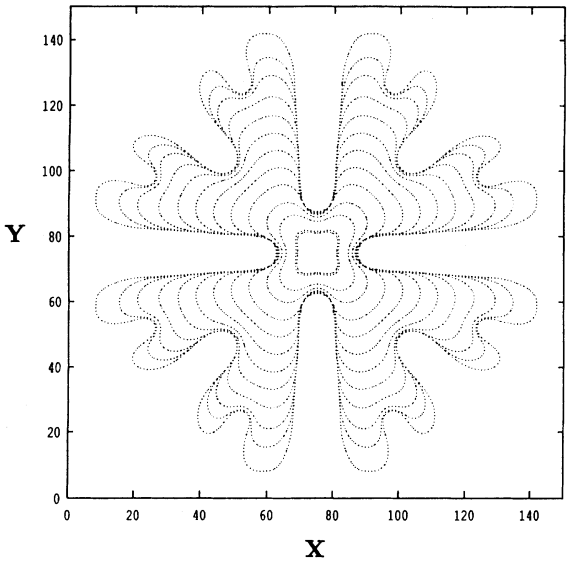

FIG. 1. Sequence of interfaces (defined as $f = 0$) for growth starting from the small square located at the center of the sample using the I_1 interaction mechanism. The noise width W is set to zero, g is held fixed temporally in an inhomogeneous manner on the square boundary of the figure, so that initially $\nabla^2 g \equiv 0$ with $g(r = 75) = 0.5$ and $g(r = 5) = 0$, the surface tension term $a = \frac{1}{2}$.

Note that the $g \approx 0$ condition behind the interface is dynamically implemented in our models. A simple interpolation procedure allows for the determination of the interface, $f = 0$, with a resolution an order of magnitude smaller than the lattice spacing.

Our principal results are summarized in Figs. 1–6. Figure 1 shows a typical pattern in the absence of noise in a circular geometry with the I_1 mechanism. This is clearly reminiscent of conventional Laplacian growth [17]. The initial square symmetry that is maintained in the present calculation is destroyed on adding an infinitesimal noise term. Note, however, that the splitting mechanism is operational even in the absence of noise. The fingering instability is seen clearly in Fig. 2(a). We have confirmed that the instability manifests itself in the exponential growth of the unstable modes with the growth rate approximately depending on the wave vector in the form suggested by Mullins and Sekerka [18]. Figure 2(b) shows a late stage of growth of a system in the planar geometry. Successive splittings of the fingers in order to maintain a characteristic finger width, screening of the lower branches by the higher ones, and the development of an intricate treelike pattern are discernible in the figure.

The basic length scale in Eqs. (1) and (2) is set by the surface tension in the form of $\sqrt{a}$. Indeed, by defining suitable length and time units, one can rescale (1) and (2) and obtain a renormalized value of $a = 1$. We have verified that the characteristic finger width in the simulations is proportional to $\sqrt{a}$ and also depends on the boundary flux rate. We find that the finger width decreases on increasing this flux approximately as the $(\text{flux})^{-1/2}$—our measured exponent is 0.45 ± 0.05 (the flux rate of g is a measure of the inverse time allowed for the diffusional

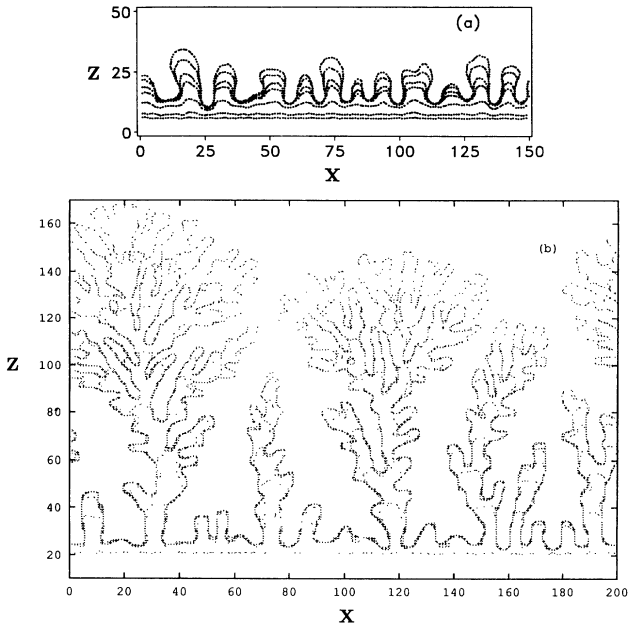

FIG. 2. (a) Initial stages of growth starting from a plane interface with the I_1 mechanism. $a = \frac{1}{4}$; $W/V = \frac{1}{4}$. The flux of the g field at the boundary was held constant during the simulation. (b) Late stages of growth of the system similar to that shown in (a).

relaxation of f near the interface) [19]. Unlike the lattice simulation of DLA processes, in our model, the interplay between the growth rate and the surface tension determines the basic finger width. Nevertheless, in the regime we have studied the fractal dimension seems to be unchanged from that obtained in lattice simulations of DLA. It is interesting to note that in solidification processes the scaling of the growth velocity as a function of the undercooling is different depending on the nature of the cutoff length scale [20]. In this context, our continuum model may be somewhat analogous to a discrete lattice diffusion transition model [21]. A key difference, however, is that the undercooling is global in the liquid state, whereas our growth processes involve diffusion of the aggregating particles from the boundary.

Figure 3 shows a typical pattern obtained in the circular geometry. A power law mass-radius relationship is found corresponding to a fractal dimension of 1.65 ± 0.05, in good agreement with that expected for a DLA cluster [2]. Figure 4 shows a pattern obtained by modifying the boundary condition to allow for a higher value of g at the boundary. The Laplacian approximation for the diffusion equation is less valid in this case. Strikingly, the pattern obtained is qualitatively different from Fig. 3 with more filling. It has not been possible to deduce the fractal dimension in this case, because of a long crossover regime. At short length scales, the effective fractal dimension is higher, but a clean power law is not obtained.

In a recent Letter, Kahanda *et al.* [9] explored the patterns obtained in the electrochemical deposition of copper at very slow rates so that local growth effects competed with the nonlocal Laplacian effects. Two distinct patterns were observed at high and low current densities. The former is a prototype of Laplacian growth phenomena and is quite similar to the patterns in Figs. 1–3. On the other hand, the latter is characterized by a columnar morphology, no sidebranching, and narrow crevices between the columns. The physical reason for this is that at low current densities the deposition rate is slowed down by a potential barrier of water molecules inhibiting the activation of cations in the double layer [9]. The growth rate then would be expected to be proportional to the density of the g field at the interface instead of the flux—a mechanism captured in I_2—[Eq. (5)]. Figure 5 shows that the fingering pattern obtained in this case bears a striking resemblance to that obtained in Ref. [9] and is qualitatively different from Fig. 2(a). The g field is no longer zero at the interface and is higher where the growth rate is larger. This in turn leads to a diffusion of g parallel to the interface causing the voids between the columns to fill in. This effect may be accentuated by

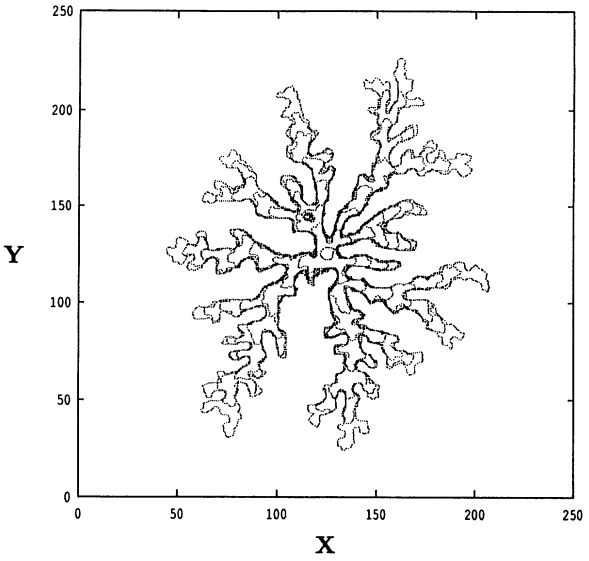

FIG. 3. Circular geometry growth with I_1 interaction mechanism. At $t = 0$ $g(r = 125) = \frac{1}{2}$ and $g(r = 3) = 0$, $a = \frac{1}{8}$, $W/V = \frac{1}{4}$. The boundary condition is as in Fig. 1.

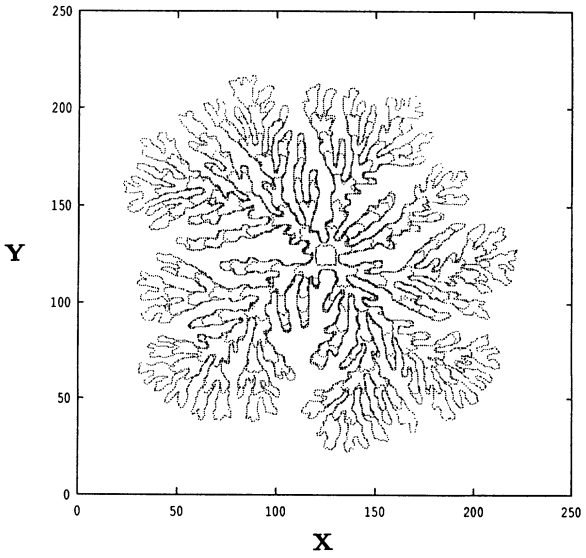

FIG. 4. Same as Fig. 3, except $g(r = 125) = 1$.

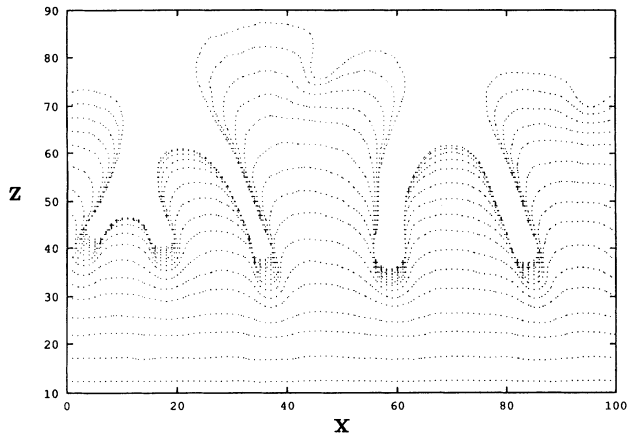

FIG. 5. Initial stages of growth starting from a plane interface with the I_2 mechanism. $a = \frac{1}{4}$; $W/V = 1$. The flux of the g field at the boundary was held constant during the simulation.

repelling the g field from the interface (as in the experiment) thus slowing the growth rate and thence allowing diffusion to smooth the g field along the interface. We have confirmed this in simulations by replacing (2) with

$$\frac{\partial g(\mathbf{r},t)}{\partial t} = \nabla \cdot (D\nabla g + Ag\nabla f) - I_2(\mathbf{r},t). \qquad (6)$$

Here, the diffusive flux has been augmented by a biased flux due to the repulsive force acting normal to the interface and in the vicinity of the interface. The neighboring fingers merge leaving holes behind (Fig. 6) and this is strikingly similar to the low current growth pattern in Ref. [9].

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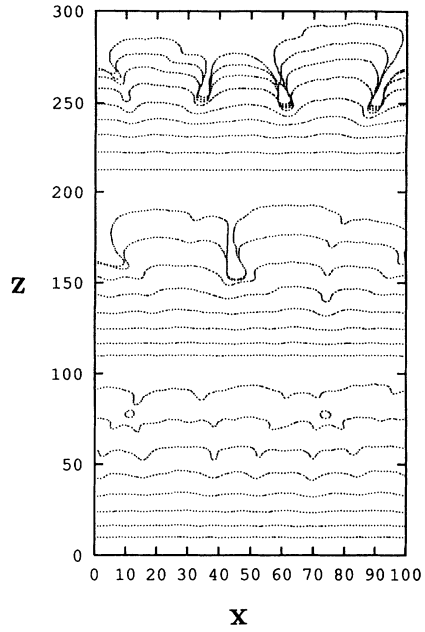

FIG. 6. Same as Fig. 5 but with an additional force repelling the diffusing particles from the growing aggregate [Eq. (6)]. The three panels show the effect of increasing the force magnitude (the force is highest for the bottom panel). The vertical coordinates of the middle and top panels have been shifted by 100 and 200 units, respectively.

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