Diffusion-Limited Fractal Growth Morphology in Thermodynamical Two-Phase Systems

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A supercritical nucleus with isotropic surface tension growing in a diffusion field is found to evolve into a fractal structure at long times and small driving forces. A newly developed numerical method using a rotated-lattice sandwich handles the anisotropy problem of the moving boundary. Scaling relations are found in agreement with a recently formulated theory.

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Growth phenomena are attracting increasing interest in all fields of science [1,2]. Despite the vast variety of possible pattern-forming phenomena there exist some universal and rather simple processes which are still poorly understood. One of them is the shape evolution of a supercritical nucleus growing in a two-phase system, for example, a crystal growing from a supersaturated solution. This is one of the simplest pattern-forming processes conceivable under essentially homogeneous nonequilibrium conditions. Surprisingly, it is still rather unclear what happens for long times in the limit of vanishing crystalline anisotropy, as in the case of a liquid droplet nucleating from a mixture of two liquids.

It has been known for about three decades [3] that such a growing nucleus becomes unstable as its radius becomes larger than a few times the critical radius. If the surface tension is anisotropic, for example due to crystalline anisotropy, it is generally believed that the nucleus finally deforms into a dendritic pattern such as a snowflake [4–6]. What happens in the limit of vanishing anisotropy, however, is much less clear.

In conventional models of diffusion-limited aggregation (DLA) atoms perform a random walk until they stick at a previously aggregated cluster [7–10]. We call these models *nonthermal* because there is no surface tension. Recent computer simulations have lead to a scaling concept [9] for this nonthermal diffusional aggregation which explains the selection of the growth rate v of the advancing envelope of a fractal interface. Surface tension, on the other hand, is present in the Saffmann-Taylor problem [11] of an inviscid fluid penetrating a viscous fluid. This case, however, is described by Darcy's law or the Laplace equation [10–14] while we discuss the fully time-dependent diffusion equation which, in principle, has much richer dynamics.

A recently proposed [15] morphology diagram relating the various patterns is based on some as yet unproven assumptions. It is the purpose of the present work to investigate the limit of vanishing anisotropy of the surface tension numerically for a nucleus growing in a diffusion field which is asymptotically homogeneous. A recent numerical investigation [16] which gave the first quantitative evidence for a morphology transition between compact dendritic and seaweed structures did not yield conclusive evidence concerning the asymptotics behavior for low noise and anisotropy.

We will now briefly describe our numerical procedure for systematically reducing the anisotropy caused by the computational grid. For simplicity we restrict ourselves to two dimensions. Details will be published elsewhere.

We discuss here the so-called one-sided diffusion model [4–6] which accounts for chemical diffusion. It is easily generalized to a two-sided model with independently definable material properties on both sides of the moving interface:

$$\frac{\partial}{\partial t}u(x,z,t)-D\nabla^2 u(x,z,t)\,, \tag{1}$$

$$u_s^0=\Delta-d_0[1-\epsilon_m\cos(m\theta)]K\,, \tag{2}$$

$$-D\hat{\mathbf{n}}\cdot\nabla u_s=v_n\,. \tag{3}$$

Equation (1) is the fully time-dependent diffusion equation (i.e., without *quasistationary* approximation [17]). Equation (2) is the boundary condition for the diffusion field u at the interface; at infinity one has $u=0$. Equation (3) is the conservation law for the solute or impurity at the interface; v_n is the normal velocity of the moving boundary. $u(x,z,t)$ is the normalized diffusion field [4,6], $\Delta\in[0,1]$ the normalized supercooling, D the diffusion coefficient, d_0 the capillary length, ϵ_m the strength of the m-fold crystalline anisotropy, and K the curvature of the interface. The Mullins-Sekerka length $\rho_{\mathrm{MS}}=2\pi\sqrt{d_0 l_D}$ is the parameter which characterizes interface instabilities; $l_D=2D/v$ is the diffusion length.

A typical problem is that a lattice introduced for the numerical treatment of the diffusion equation (1) automatically introduces some anisotropy, even for $\epsilon_m=0$ in (2). The basic idea for reducing this undesirable anisotropy is to use a rotated-lattice sandwich constructed in the following way. We first define an outer frame which consists of a channel formed by two rigid sidewalls. The deformable moving boundary runs across the channel and the distant fourth boundary is kept straight but mobile. The diffusion field responsible for the structure formation of the moving boundary acts only inside this frame. Concepts like a random self-adaptive grid of anchor points for the diffusion-field [18] or grid-generation methods popular in finite-element calculations [19] turned out to be too

time consuming. Other methods with a sharp interface [20,21] or a phase field model [22,23] have also not succeeded in producing definite results up to now. Our procedure is to map this frame onto two or more independent regular lattices which are shifted by irrational amounts and rotated against each other. Most of the simulations were performed on a stack of four lattices leaving no four- or eightfold anisotropy; even higher-order anisotropy was not detected within our numerical accuracy.

At each time step we solve the diffusion equation on all lattices independently using the boundary conditions along the frame and then calculating the diffusion flux at the moving boundary. For this purpose, a curvilinear set of curves parallel to the boundary at fixed distance is used. On this set, the values of the diffusion field are obtained by interpolation from the underlying lattice. We then locally advance the moving boundary independently on all lattices and average the resulting new boundary position over all lattices.

A circular geometry for the moving boundary is even simpler to realize. Channel geometry turned out to be superior for good statistics and for comparison with recent predictions [15]. The moving interface was always kept approximately at the center of each lattice. We have performed numerous tests, for both circular and channel geometry, with and without surface tension, as well as with and without anisotropy. For constant growth rates the stationary results agreed within a few percent with our previous simulation results based on a (by definition) fully isotropic Green's function method [17] in quasistationary approximation. The speed of both methods is comparable for the same resolution, although there is somewhat more noise produced by the present fully time-dependent scheme.

In particular, we confirm the recently reported [24] transition from symmetrical to parity-broken fingers [Fig. 1(a)] in channel geometry (note the difference between time-dependent and Laplacian growth in this case [25]), and we also confirm the scaling behavior of free dendritic growth with anisotropy [25,26] down to capillary anisotropies $\epsilon_m = 0.05$ (in agreement with Ref. [17]). The parity-broken finger appears to represent a branch of solutions which moves significantly faster than the corresponding dendritic solutions in the channel, even at nonzero but small anisotropy.

In Fig. 1(b) we present a snapshot from a long-time simulation of a moving boundary in a channel, but in contrast to Fig. 1(a), now with periodic boundary conditions. In the center one clearly sees structures similar to Fig. 1(a), as if two parity-broken dendrites try to stabilize each other. We call this *compact seaweed:* "Seaweed" because of missing anisotropy and "compact" since there is no indication of "fractality" as discussed below. The structure selects a unique velocity and an associated characteristic length for the pattern independent of the channel width (for sufficiently wide channels), as predicted by a recent conjecture [15]. For $\Delta \gtrsim 0.6$ the characteristic length should be of the order of the stability length ρ_{MS}, which is consistent with our findings. A detailed test of the predicted variation [Eq. (11) of Ref. [15]] with Δ near 0.5 was not yet possible because of extreme requirements of computing time and storage.

Fractal seaweed patterns were predicted [15] to occur at supercoolings below $\Delta \approx 0.5$, advancing at a well-defined average growth rate. A true fractal object, of course, can only occur on infinite structures which means infinite diffusion length $l_D \to \infty$. Our numerical results (Fig. 2) are consistent with the existence of such fractals over a finite range, as in the case [9] of lattice aggregates

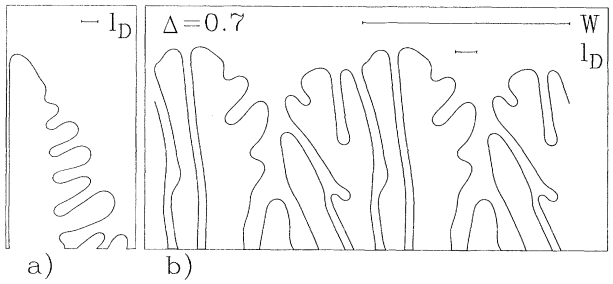

FIG. 1. (a) Parity-broken finger growing from a time-dependent diffusion field in a wide channel with *reflecting* conditions on the sidewalls. A growth rate is selected essentially independent of the channel width W; the sidebranches occur at the same wavelength as on an anisotropic dendrite growing at the same velocity. (b) Channel growth with periodic boundary conditions at the walls. Structures like the parity-broken fingers in (a) are visible inside this compact seaweed pattern. The diffusion length here is only about 10% of the channel width. The growth rate is only 15% slower than in (a). This supports the idea [15] of a growth rate selection mechanism intrinsic to the pattern. Parameters were $D=1$, $\Delta=0.7$; (a) $d_0=0.375$, $W=300$, $l_D=38$; (b) $d_0=0.434$, $W=478$, $l_D=50$. All lengths are given in lattice units; lattice size $=1121\times1121$.

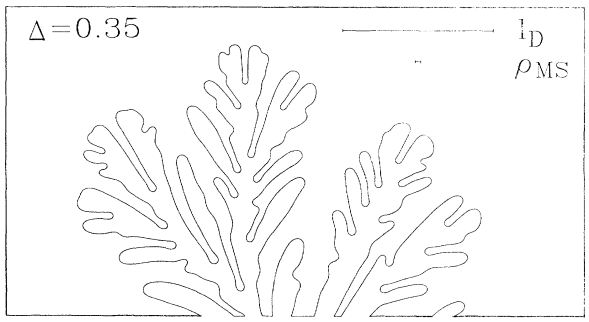

FIG. 2. Fractal growth pattern in a wide channel (relative to the diffusion length) at low supercooling. Parameters were $D=1$, $\Delta=0.35$, $d_0=0.0068$, $W=700$, $l_D=182$. The width of the narrow troughs is about equal to the Mullins-Sekerka length.

in the nonthermal model. The diffusion length l_D again was small compared to the channel width W. Our control parameters were supercooling $\Delta=0.35$, isotropic capillary length $d_0=0.0068$, and $\epsilon_m=0$. We therefore can assume that the central part of the moving interface is essentially unperturbed and behaves just like an initially circular surface of a growing nucleus after very long time.

The local fractal dimension as a result of a box-counting analysis of this pattern is shown in Fig. 3. To minimize boundary effects, only the central third of the channel was used. Both at small and large length scales one expects a value of 2: On small scales the interface looks smooth; there are no structures smaller than the stability length ρ_{MS}. On large scales, one has a constant average density. On intermediate scales one sees a fractal dimension of about $D_f \approx 1.73$ which consequently should be taken as an upper bound for the fractal dimension to be obtained in the limit $l_D \to \infty$. A similar analysis for the length of the moving boundary yields a fractal dimension $D_f^p \approx 1.66$ as the fractal dimension of the perimeter of the growing structure.

This analysis is furthermore supported by comparison with the recently proposed [15] scaling equation for dependence of the growth rate v on the supercooling Δ and effective noise Γ (the dimensionless Γ measures the relative amplitude of interface fluctuations in units of wavelength ρ_{MS}):

$$v \sim D/d_0 |\ln\Gamma|^{-2} \Delta^{\psi}, \quad \psi = 2/(2-D_f) . \tag{4}$$

The observed velocities of the leading tip at three different values $\Delta=0.35$, 0.393, 0.44 for the supercooling can be matched with an exponent $\psi \approx 6.0$, from which one obtains with the help of (4) a fractal dimension $D_f(\text{scaling}) \approx 1.66$. A conjectured universal value $D_f = 1.71$ would give $\psi \approx 7$, while the scaling of the nonthermal model [9] would suggest $\psi \approx 3.5$. Clearly, our results favor Eq. (4), which follows from the concept of a velocity-dependent small-scale cutoff [15] for the scaling region. Admittedly there are some uncertainties in our values for the fractal dimensions. In any case they obey the inequality $D_f^p \leq D_f$ and $1.66 \leq D_f \leq 1.73$. Within this uncertainty our result is quite consistent with a value $D_f \approx 1.71$ obtained for the fractal dimension [8] of a 50 million particle cluster of nonthermal aggregation in isotropic space.

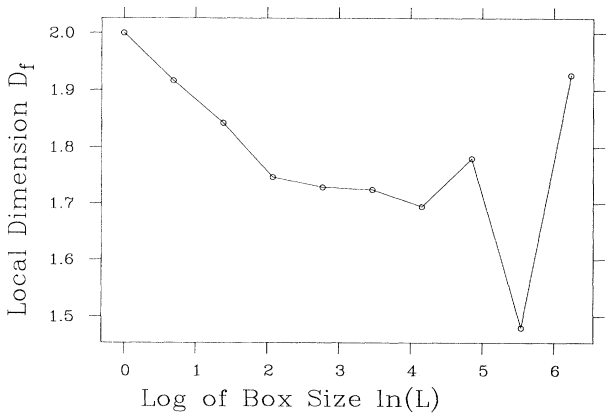

FIG. 3. Local fractal dimension $D_f(L)$ from box-counting analysis of the fractal patterns (like in Fig. 2) plotted vs the logarithm of the box size L. Symbols correspond to doubling of box size. The central plateau extends laterally over more than an order of magnitude and gives a fractal dimension of $D_f \approx 1.73$.

Finally we made an attempt to estimate the strength of the effective noise $|\ln\Gamma|$ entering (4). The space and time discretization of the interface motion is a source of noise which was not directly considered previously [15]. For parameters such as those used in Fig. 2, we estimated $|\ln\Gamma|$ to be of order unity according to amplitudes of side-branches of simulated dendrites. This agrees with the value needed to match the amplitude in (4) with the data. This is consistent with the predictions [15]; it does not, of course, exclude the possibility that the fluctuations leading to the irregular fractal shapes are also of intrinsically dynamical origin as assumed for the high-speed region. Because of the substantial computing requirements needed to finally check the scaling exponent of the noise in (4) we must leave that point open at present.

In summary, we have found in our numerical simulation of a two-dimensional droplet growing in a diffusion field that it evolves into a structure at long times which may be characterized as a finite-range fractal object at low values of the supercooling. Its fractal dimension seems to agree with the fractal dimension observed for atomistic nonthermal Laplacian growth supporting a recent conjecture [15] about universality. This seems to be the first observation of such a fractal growth process in an isotropic system close to thermal equilibrium.

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