Role of noise in the initial stage of solidification instability

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Evolution of the morphological instability at the initially flat interface of a nonfaceting crystal growing freely into its pure melt has been studied by a computer simulation. A stochastic differential equation for the spatial Fourier components of the interface was formed by adding Gaussian random-noise terms representing spontaneous temperature fluctuations to the deterministic Mullins-Sekerka result of linear stability analysis. The results of the simulation qualitatively reproduce recent experiments in succinonitrile in which the spatial Fourier spectrum was found to be extremely noisy. The noise level required in the simulation was found to agree qualitatively with a rough estimate of temperature-fluctuation effects.

Nonequilibrium dynamical systems frequently undergo pattern-forming instabilities resulting in the appearance of complex spatial structures in an initially structureless medium. The best known examples occur in hydrodynamics, e.g., the Rayleigh-Benard and Couette-Taylor instabilities.[1] Pattern-forming instabilities also occur at interfaces, such as the viscious fingering instability, aggregation, or dendritic solidification.[2,3]

A fundamental question in the analysis of pattern formation arises when one considers how the process is initiated. In the case of the Rayleigh-Benard instability, for example, hydrodynamics leads to an evolution equation for the amplitude A (whose square is the convective heat current) of the form

$$\frac{dA}{dt}=C_1 A - C_3 A^3 + C_5 A^5 \cdots , \qquad (1)$$

where C_1 increases from negative to positive as the temperature gradient is increased through the critical value for onset of convective flow. Once C_1 becomes positive, the quiescent system ($A=0$) is unstable, but convection cannot begin in this deterministic description since $dA/dt=0$ as long as $A=0$, even if $C_1>0$.

Recently, Meyer *et al.* have converted Eq. (1) to a stochastic differential equation by adding a Gaussian zero-mean random-noise term f to the right-hand side.[4] The onset of convective flow was then modeled with a computer simulation in which a new value of f is inserted at each iteration, and the result was shown to give an excellent fit to the experimentally observed evolution of convective flow, although the noise level required by the simulation is 4 orders of magnitude larger than predicted by hydrodynamic fluctuation theory.

The role of noise has also been shown to be crucial to the growth of side branches during dendritic crystal growth of NH_4Br from solution. Dougherty *et al.* have recently shown that the side branch amplitude grows exponentially with distance from the dendritic tip, apparently as a result of amplification of microscopic noise involving concentration fluctuations in the solution near the tip.[5]

We have recently reported a preliminary quantitative study of the morphological instability at the initially planar interface of a nonfaceting crystal (succinonitrile) growing into its pure melt.[6] Mullins and Sekerka[7] first carried out a linear stability analysis for this problem 25 years ago and found that the evolution of a small sinusoidal perturbation of amplitude A_k and wavelength $2\pi/k$ on the planar interface of a crystal advancing into its pure undercooled melt with velocity v_0 is given by

$$\frac{dA_k}{dt}=\omega_k A_k . \qquad (2)$$

The linear growth coefficient ω_k is given (approximately) by

$$\omega_k = v_0 k(1-d_0 l k^2) , \qquad (3)$$

where d_0 and l are the capillary length and the thermal diffusion length, respectively. Equations (2) and (3) show that the interface is unstable against fluctuations spanning the range of k values $0 \le k \le (d_0 l)^{-1/2}$. Note, however, that Eq. (2), like Eq. (1), is purely deterministic.

Our experiments resulted in a sequence of high-resolution digitized records of the advancing initially planar interface as shown in Fig. 1 (note that the y axis in Fig. 1 is expanded by $10\times$). Spatial Fourier transformation of the three records shown in Fig. 1 resulted in the spectrum of Fourier amplitudes A_k shown in Fig. 2. The growth of Fourier amplitudes in a restricted range of k values is in qualitative (but not quantitative) agreement with the Mullins-Sekerka prediction.[6,8] But the large variation of A_k between neighboring k values indicates the importance of noise in the early evolution of the instability.

We have introduced stochastic noise terms into the Mullins-Sekerka analysis, in analogy with the approach of Meyer *et al.*[4] to the Rayleigh-Benard problem, by rewriting Eq. (2) as a set of stochastic differential (or Langevin) equations:

$$\frac{dA_k}{dt}=\omega_k A_k + f_k(t) , \qquad (4)$$

where the noise terms $f_k(t)$ are assumed to be white with respect to both k and t, i.e.,

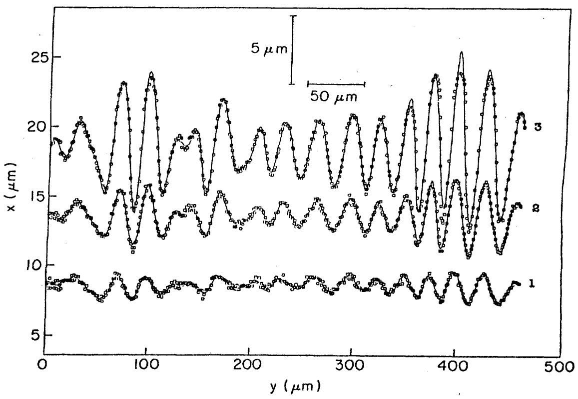

FIG. 1. Experimentally observed profiles $x(y)$ of the growing crystal-melt interface of succinonitrile at three different times. The time interval between each successive curve is 1 sec, and curve 3 corresponds to about 20 sec after the start of quenching. The solid lines through the data points are 10-point least-squares cubic B-spline fits. Note that the y axis has been expanded by 10× as shown by the inset vertical and horizontal bars.

$$\langle f_k(t) f_{k'}(t') \rangle = 2s^2 \delta_{kk'} \delta_{tt'} \ . \tag{5}$$

This method of including a stochastic source into an otherwise deterministic system has been used by other workers in addition to the reference mentioned above. Cook,[9] in his contribution to the Hilliard-Cahn-Cook theory for the early stage of spinodal decomposition, used an evolution equation for the composition modulations that is mathematically identical to Eq. (4). From that equation, he was able to explain successfully the fluctuations in the system observed experimentally through x-ray spectroscopy. More recently, Toral *et al.*[10] worked on the same spinodal system by numerical simulation. Their approach was again similar to our, i.e., they started with a deterministic equation that described the dynamics of the system; then a stochastic term was added to account for the effect of noise.

In our computer simulation, the set of 38 Eqs. (4), for $0<k<0.1$ μm^{-1} (corresponding to k steps of $\delta k = 0.00266$ μm^{-1}) was analyzed, starting with all $A_k = 0$ as the initial conditions. At each step, a new set of random-noise terms $f_k(t)$ was selected following a zero-mean Gaussian random distribution, and the amplitudes $A_k(t)$ were obtained by numerically integrating the set of Eqs. (4). The rms value of the noise (s) is the only adjustable parameter in the simulation. The result of one such simulation, with time steps of 0.52 sec, is shown in Fig. 3. The lower and upper curves correspond to times of 2.5 and 20 sec, respectively. The rms noise level, chosen to approximately match the experimental results of Fig. 2, was $s = 0.037$ μm/sec. Note that the envelope of the lower curve is essentially flat, showing that at early times the evolution of all Fourier components is governed by the stochastic noise terms and the deterministic terms play no role. The shape of the upper curve shows that once the deterministic terms become important, the Fourier components with large linear growth coefficients are selectively amplified, leading to an envelope conforming with the Mullins-Sekerka theory (shown as the dotted smooth line in Fig. 3), but the influence of the stochastic terms remains in the obvious noisiness of the spectrum.

The time evolution of a particular mode can be followed on the logarithmic plot of $|A_k(t)|$ with $k = 0.03$ μm^{-1} as shown in Fig. 4. At early times, A_k follows a random walk growth. At a "crossover" time τ, exponential growth sets in, as indicated by the solid line whose slope represents the Mullins-Sekerka prediction of Eq. (2). We have found that the value of τ does not depend on the rms noise level, although the exponential growth line on the log plot is displaced upward as the noise level increases. We also find that τ is inversely proportional to the linear growth coefficient ω_k.

We believe that the source of the stochastic noise represented by $f_k(t)$ in Eq. (4) is temperature fluctua-

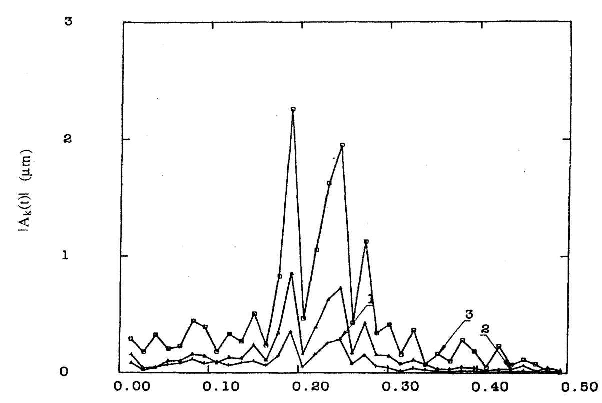

FIG. 2. Modulus of Fourier coefficients $A_k(t)$ of experimental data of Fig. 1. Curves 1, 2, 3 in this figure correspond to curves 1, 2, 3 of Fig. 1.

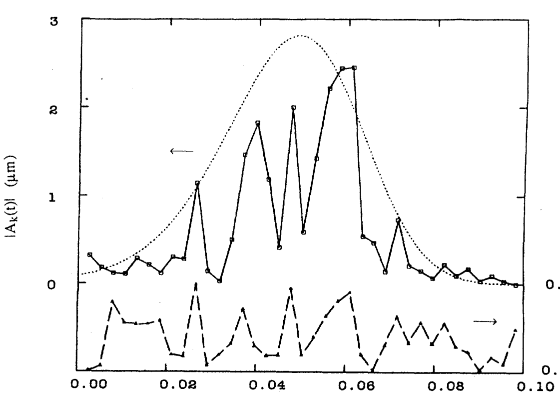

FIG. 3. Modulus of Fourier coefficients of the interface from the computer simulation. The lower and upper data points correspond to 2.5 and 20 sec after initiation ($A_k = 0$, $t = 0$). The smooth dotted line at the top is the prediction of the Mullins-Sekerka theory assuming a uniform starting amplitude for all k of $A_k = 0.015$ μm at $t = 0$. The rms noise $s = 0.037$ μm/sec. Note the different scales in amplitude for the two different times.

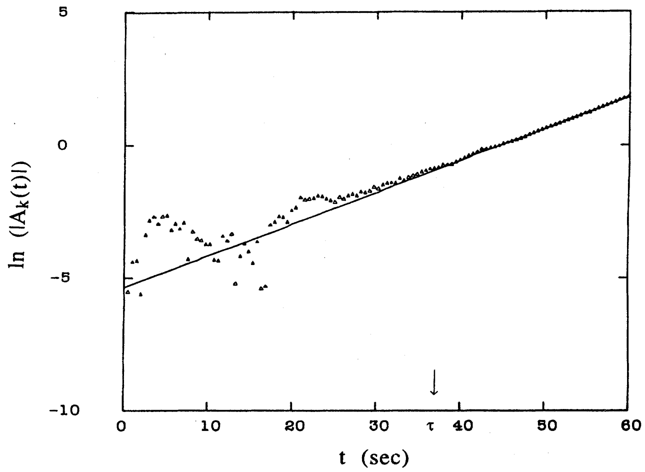

FIG. 4. Logarithm of the modulus of $A_k(t)$ for the $k=0.03$ μm^{-1} mode vs time. The straight solid line is a fit through the last 30 data points. Its slope agrees with the prediction of the Mullins-Sekerka theory.

tions. Since succinonitrile is nonfaceting with linear growth kinetics, a temperature fluctuation ΔT should produce a fluctuation in growth velocity $\Delta v = -\Psi \Delta T$. Ψ is the kinetic coefficient which, for succinonitrile, has been reported to be $\Psi = 17$ cm/sec K.[11] Thus we expect that

$$f_k(t) = \Psi(\Delta T)_k , \tag{6}$$

where $(\Delta T)_k$ is the kth Fourier component of (ΔT).

We have not attempted to carry out a serious calculation of $(\Delta T)_k$ for several reasons. One clear reason is that our computer simulation assumes that all $(\Delta T)_k$ have a persistence time of one iteration (0.52 sec) while the actual correlation time for temperature fluctuation is k dependent, with $t_k = (D_T k^2)^{-1}$ where D_T is the thermal diffusion constant.

As a rough approximation, we can compute the temperature fluctuation in a volume element of size $(1/k_c)^3$ where k_c, the maximum wave vector (or shortest wavelength) fluctuation against which the system is unstable, is given by Eq. (3) as $k_c = (d_0 l)^{-1/2} = 0.085$ μm^{-1}.

The mean-square temperature fluctuation in a volume element ΔV is given by thermodynamic fluctuation theory as

$$\langle (\Delta T)^2 \rangle = \frac{k_B T^2}{C_p \Delta V} , \tag{7}$$

where C_p is the specific heat and k_B is Boltzman's constant. Equations (6) and (7), with $\Delta V = (1/k_c)^3$, then give $\Delta v = \Psi \Delta T = 0.23$ μm/sec which is about six times larger than the value 0.037 μm/sec deduced from the simulation.

In summary, we have shown that the very noisy Fourier spectrum of the interface morphology observed in succinonitrile in the early stages of the Mullins-Sekerka morphological instability can be successfully explained by a computer simulation in which the deterministic Mullins-Sekerka equation is supplemented with stochastic noise terms which describe spontaneous temperature fluctuations at the interface. Additional studies of this system are in progress.

Note added in proof. We have recently carried out a more rigorous calculation of the strength of the noise terms in Eqs. (4) and (5) based on microscopic fluctuation theory in which a Landau-Lifshitz fluctuating heat flux was introduced *ab initio* into the energy conservation equation. The estimated noise strength was found to be 1.0×10^{-7} μm/(sec)$^{1/2}$, 5 orders of magnitude smaller than the result $S_0 = S(\Delta t)^{1/2} = 2.7 \times 10^{-2}$ μm/(sec)$^{1/2}$ found from the computer simulation. This discrepancy closely resembles the result of Ref. 4.

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