

Stability of incomplete explosive crystal growth

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We study a model of explosive crystallization of an amorphous thin film in which the film is not necessarily crystallized completely. We assume instead that only a fraction of the film crystallizes, and that this fraction depends on the local temperature at which the transition takes place. Steady states of the model can be found in the same way as in the case when the transition is assumed to go to completion. In addition, the linear stability analysis of these steady states is simply related to that with complete crystallization: A single new parameter appears which measures the sensitivity of the rate of latent heat release to the temperature at the transition front, and the theoretical parameters on which the stability depends are rescaled by this new parameter. If the rate of latent heat release actually decreases as the interface temperature increases, then the steady state is always linearly stable. Similar results can be obtained for laser-driven growth.

I. INTRODUCTION

Explosive crystallization is a process in which a sample of amorphous material is transformed into a crystalline state, with the transition largely, if not totally, activated by its own latent heat. More specifically, once some energy has been injected from outside to trigger the transition, the latent heat released as amorphous material crystallizes locally can provide the activation energy needed to crystallize nearby amorphous material, thereby driving a boundary between still-amorphous and now-crystalline regions across the sample. Experiment has shown that initially uniform amorphous films which are crystallized explosively often develop undulations in thickness as the transformation takes place, with the undulations forming ridges or "rolls" whose long axes are perpendicular to the direction in which the crystallization front moved.¹⁻⁴ The spacing between adjacent rolls is of the order of the ratio of the thermal diffusion constant of the film to the average speed of the transition front.^{2,3} Thus these undulations have been connected theoretically with a thermal instability in which the local temperature at the transition front varies periodically in time.⁵⁻⁸ These oscillations have been seen in numerical simulations of explosive crystal growth,⁵⁻⁷ and are also predicted by a linear stability analysis⁶⁻⁸ of crystallization with a constant front velocity.

The usual theoretical model of explosive crystallization, which was originally proposed by Gilmer and Leamy⁹ and independently by Shklovskii,¹⁰ incorporates heat diffusion in the plane of the film, latent heat release at the amorphous-crystalline boundary, and interface kinetics via a nontrivial dependence of the local velocity of the boundary on its temperature. However, it assumes that the amount of latent heat released when a portion of the amorphous film crystallizes is simply proportional to the area of that portion. This is equivalent to assuming that the crystallization is complete, or at least that a constant fraction of the initially amorphous material crystallizes. On the other hand, there is experimental evidence, both

for self-sustained³ and laser-driven⁵ growth, that the fraction of material which crystallizes is not constant, but rather varies periodically with the same spatial period as the surface undulations have; in fact, the variation in the amount of remaining amorphous material is partially the cause of the surface undulations.⁵⁻⁸ Existing theoretical treatments⁵⁻⁸ neglect these variations in order to calculate the temporal period of the thermal oscillations at the transition front, and then invoke them in order to connect these oscillations with the production of surface undulations. Zeiger *et al.*⁵ have suggested that the variation in the crystallized fraction may affect the interface motion, but they have not explored the possibility.

In this paper we will include in the analysis of the thermal instability the variation in the fraction of material which crystallizes. Since the distribution of remaining amorphous material in a crystallized film is seen to be periodic, it is reasonable to model this fraction as a function of local boundary temperature. (In fact, it turns out to be more convenient to write it as a function of the boundary velocity, which is itself modeled as a function of temperature.) We find that steady states describing an amorphous-crystalline boundary advancing at a constant speed can be found by the same method as that used by van Saarloos and Weeks^{6,7} in their analysis of the model with complete crystallization. Furthermore, the linear stability analysis of these steady states is almost identical to that carried out by van Saarloos and Weeks^{6,7} for the one-dimensional problem and by Kurtze, van Saarloos, and Weeks⁸ for the multidimensional problem. A single new parameter η appears, which is the logarithmic derivative of $v f(v)$, where $f(v)$ is the fraction of amorphous material which crystallizes when the interface is advancing at velocity v . We show that the old theoretical parameters β and α , which are related to the boundary velocity and the nonequilibrium growth kinetics, respectively, are replaced in the stability analysis by β/η and $\alpha\eta$, and the growth rates and wave numbers of perturbations are multiplied by η and $\eta^{1/2}$, respectively. Thus unless $f(v)$ decreases more quickly than $1/v$ as v increases, so that η is

negative, there is no qualitative change in the stability; only the onset of instability is shifted, and the spacing of the resulting undulations is altered. Furthermore, if η is zero or negative, which means that the actual rate at which latent heat is being released decreases as the front velocity increases, then we find that the steady state is always linearly stable. We also obtain similar results for the case of crystallization driven by a laser slit.^{5,8}

In the following section we present the model equations we will analyze, and review how steady-state solutions of these equations can be found. Section III contains the linear stability analysis of the steady states, and shows how the stability equation can be transformed, by a suitable rescaling of parameters, into the equation derived and analyzed for complete crystallization by Kurtze, van Saarloos, and Weeks. Finally, in Sec. IV the results are discussed and related to other types of phase transitions which can be described by moving boundary problems.

II. MODEL EQUATIONS AND STEADY STATES

We will consider a boundary between amorphous and crystalline regions which moves at a local normal velocity V^b across a thin, initially amorphous film. Following Gilmer and Leamy,⁹ we write a diffusion equation for the local temperature $T(x,y,t)$ of the film, in a frame of reference moving with velocity V in the x direction:

$$\frac{\partial T}{\partial t} = D\nabla^2 T + V \frac{\partial T}{\partial x} - \Gamma(T - T^0) + (L/c)V^b f(V^b) \delta(x - x^b). \quad (2.1)$$

Here D is the thermal diffusion constant of the film, L is the latent heat of crystallization, c is the specific heat of the material, T^0 is the ambient temperature, and Γ is a phenomenological damping parameter which models heat loss to the environment. The position x^b of the amorphous-crystalline boundary, and hence its normal velocity V^b , can depend on y and t ; the most interesting theoretical part of the problem is to determine what this dependence is. We can take the average velocity of the boundary to define the x direction. The function $f(v)$, as discussed in the introduction, is the fraction of amorphous material which crystallizes when the boundary is moving at a speed v . (There is actually a geometric factor involving the square of the slope of the boundary which should appear in the δ -function term in this equation, but since we will only be concerned with the linear stability of a straight-line interface, and this term is *quadratic* in the interface slope, we will not bother to write it here, even though it would be necessary for a correct nonlinear analysis.) The velocity of the amorphous-crystalline boundary is determined, via nonequilibrium interface kinetics, by the local temperature T^b at the boundary; we take this effect into account by postulating the existence of an intrinsic growth-rate relation,

$$V^b(y,t) = V^b(T^b(y,t)), \quad (2.2)$$

which gives the normal velocity of the boundary at any point along it in terms of the temperature there. Unlike for crystallization from an undercooled melt, this function

is generally increasing—typically an Arrhenius function—for crystallization from the amorphous phase. These two equations, together with the boundary condition $T = T^0$ far from the boundary, complete the specification of the moving boundary problem.

A steady-state solution of these equations represents an amorphous-crystalline boundary which maintains its shape while advancing in the x direction at a speed V . To find a simple steady state, we assume that the boundary is a straight line, which by definition is the y axis. The normal velocity of the boundary is then identically equal to V . The diffusion equation reduces to a one-dimensional problem; its solution is

$$T(x,y,t) = T_{SS}(x) = T^0 + (L/c)\beta^{1/2}f(V)\exp\left[-\frac{V}{2D}(x + \beta^{-1/2}|x|)\right], \quad (2.3)$$

where, following van Saarloos and Weeks, we have defined the parameter

$$\beta = \beta(V) = V^2 / (V^2 + 4D\Gamma), \quad (2.4)$$

which is a dimensionless measure of the steady-state boundary velocity (or of the importance of heat loss) which always lies between 0 and 1. In order for this solution to exist, we must have chosen the speed V of our reference frame so that the boundary velocity $V^b = V$ and temperature T^b are consistent with the intrinsic growth-rate relation (2.2). The resulting equation can be written in the form

$$T^b(V) = T^0 + (L/c)\beta^{1/2}f(V), \quad (2.5)$$

where we have inverted the relation (2.2) to write the boundary temperature T^b as a function of its velocity V^b . In practice, if this relation and the dependence of $f(v)$ on v are known, then the boundary velocity is found by plotting the two sides of this equation, the growth-rate curve and the steady-state curve respectively, and looking for intersections of the two. We will find that the stability of the steady state depends on the relative slopes of the two curves at their intersection.

III. LINEAR STABILITY ANALYSIS

We now look at the stability of the steady-state solution (2.3)–(2.5) of the model against infinitesimal perturbations. To do this, it is convenient first to change to dimensionless variables, scaling all lengths and times by the diffusion length $2D/V$ and diffusion time $2D/V^2$, and temperature by L/c . We then write the infinitesimal perturbation of the steady state in the form

$$x^b(y,t) = \epsilon \exp(iky + \omega t), \quad (3.1)$$

$$T(x,y,t) = T_{SS}(x) + \hat{T}(x)x^b,$$

insert this into the diffusion equation (2.1), and linearize in the amplitude ϵ of the perturbation. Three dimensionless parameters arise naturally in this calculation. One is the parameter β defined in Eq. (2.4) above. A second,

$$\alpha = [(L/c)\beta^{1/2}f(V)/V](dV^b/dT^b)|_{SS}, \quad (3.2)$$

measures the sensitivity of the growth rate to the local boundary temperature; for $f=1$ it is the same as the parameter α introduced by van Saarloos and Weeks. The new parameter which appears measures the sensitivity of the crystallized fraction to the boundary temperature or velocity:

$$\eta = d \ln[vf(v)]/d \ln v|_{v=v}. \quad (3.3)$$

The basic equation which reveals the stability or instability of the steady state arises when we calculate the correction $\hat{T}(0)x^b$ to the boundary temperature and relate it via the growth-rate curve to the shift ωx^b in the boundary velocity. After a certain amount of algebra (similar to that presented in Ref. 8), we obtain the equation

$$(\omega + \alpha)(1 + \beta k^2 + 2\beta\omega)^{1/2} = \alpha(\eta\omega + 1), \quad (3.4)$$

where we must choose the branch of the square root which has a positive real part. This equation is very similar to the stability equation derived by Kurtze, van Saarloos, and Weeks⁸ for the case of complete crystallization, for which we would have $\eta=1$. In fact, if we rescale space and time by setting

$$\begin{aligned} k' &= k\eta^{1/2}, \\ \omega' &= \omega\eta, \end{aligned} \quad (3.5)$$

and define the new parameters

$$\begin{aligned} \alpha' &= \alpha\eta, \\ \beta' &= \beta/\eta, \end{aligned} \quad (3.6)$$

then the stability equation (3.4) becomes

$$(\omega' + \alpha')[1 + \beta'(k')^2 + 2\beta'\omega']^{1/2} = \alpha'(\omega' + 1), \quad (3.7)$$

which is *exactly* the stability equation in Ref. 8 with α , β , ω , and k replaced by the rescaled parameters α' , β' , ω' , and k' (and the capillary parameter d_0 and the laser parameter R set equal to zero). Thus we may carry over to the present problem the following conclusions reached by Kurtze, van Saarloos, and Weeks for complete one- or two-dimensional self-sustained explosive crystallization:

(1) The steady state is linearly unstable with a real growth rate ω for $\alpha' > (1 - \beta')^{-1}$ or $\alpha > (\eta - \beta)^{-1}$. As in the case of complete crystallization this means that in order for a steady state to be linearly stable, the slope dv/dT of the steady-state curve must be greater than that of the intrinsic growth-rate curve at their intersection. Thus in general if there are two solutions of Eq. (2.5) for the allowed steady-state boundary velocities, the one having the lower velocity will correspond to a steady state which is linearly unstable.

(2) The steady states having $\alpha' < (1 - \beta')^{-1}$ are not necessarily linearly stable. For $\beta' < [(\alpha')^2 - 1]/4\alpha'$ or $\beta < (\alpha^2\eta^2 - 1)/4\alpha$, there is an oscillatory instability of the steady state with wave vector $k=0$. Thus steady states in this range of parameters will give way to oscillations in which the boundary can remain a straight line, but its velocity will vary periodically in time. The angular frequency of this oscillation is given by the imaginary part of

the growth rate ω of the instability; at the threshold this is given by

$$\omega' = i\alpha'[(\alpha' - 3)/(\alpha' + 1)]^{1/2}$$

or

$$\omega = i\alpha[(\alpha\eta - 3)/(\alpha\eta + 1)]^{1/2}.$$

(3) For a multidimensional system, morphological instabilities, for which the wave number of the marginally unstable mode is nonzero, occur for $\beta' < \alpha'/4$ or $\beta < \alpha\eta^2/4$. When this occurs, the boundary will not remain straight, but will acquire a wavy shape which itself oscillates as it advances across the sample. At the onset of this instability, the wave number of the unstable perturbation is given by $(k')^2 = (2\beta' - 1)/\beta'$ or $k^2 = (2\beta - \eta)/\beta\eta$, and its growth rate by

$$(\text{Im}\omega')^2 = 8\beta'(2\beta' - 1)$$

or

$$(\text{Im}\omega)^2 = 8\beta(2\beta - \eta)/\eta^4.$$

The results of the linear stability analysis are radically different if η is zero or negative. To see this we first note that the onset of all instabilities in the α - β plane scale in the α direction as negative powers of η . Thus as η goes to zero, no instabilities occur for finite α . In fact, this persists for negative η (provided α is positive), as we will now show. First, we write the square root in the original stability equation (3.4) in terms of its real and imaginary parts,

$$(1 + \beta k^2 + 2\beta\omega)^{1/2} = Q + iR, \quad (3.8)$$

where Q and R are real and Q must be nonnegative. We are actually interested in locating solutions of (3.4) for which ω is purely imaginary (or zero); in these cases we have

$$\begin{aligned} 1 + \beta k^2 &= Q^2 - R^2, \\ \beta\omega &= iQR, \end{aligned} \quad (3.9)$$

and so the stability equation becomes the pair of real equations

$$\begin{aligned} \alpha Q - QR^2/\beta &= \alpha, \\ \alpha R + Q^2R/\beta &= -\alpha|\eta|QR/\beta. \end{aligned} \quad (3.10)$$

Since α , β , and Q are all nonnegative (in fact Q must be at least as large as 1), we see that the second equation in (3.10) can only be satisfied for $R=0$. This then leads to $Q=1$ from the first equation in (3.10), and $k=0$ and $\omega=0$ from (3.9). Thus there can be no oscillatory instability for nonpositive η . Furthermore, the solution we have just found with $\omega=0$ is a Goldstone mode, which reflects the invariance of the physical situation with respect to changes in the definition of $x=0$. In order to see whether there is actually a mode of instability which has $\omega=0$ with $k=0$, we square the stability equation (3.4) with $k=0$ to obtain

$$2\beta\omega^3 + (4\alpha\beta + 1 - \alpha^2 |\eta|^2)\omega^2 + 2\alpha(\alpha\beta + 1 + \alpha |\eta|)\omega = 0. \quad (3.11)$$

From this, we see that the Goldstone mode $\omega=0$ satisfies the equation identically. A second solution with $\omega \geq 0$ could only occur if the coefficient of ω were to vanish or become negative, but this coefficient is at least as large as 2α . In general, if the coefficient of ω^2 becomes negative, then there will also be solutions of (3.11) having positive real part, but these are unimportant, since they lead to solutions of (3.4) in which the square root has a *negative* real part. Thus we see that if the rate of latent heat release *decreases* with increasing boundary velocity or temperature, then the instability of the steady state is suppressed completely.

IV. DISCUSSION

From the calculations above, we see that the effect of incompleteness of the transition on the stability of explosive crystal growth is merely to rescale the theoretical parameters in the problem by a parameter η , defined in (3.3), whose deviation from unity measures the sensitivity of the crystallized fraction to the temperature at which the transition takes place. Since the rate at which latent heat is being released when the amorphous-crystalline boundary is advancing at a speed v is $(L/c)vf(v)$, negative η means that the amount of latent heat being released at the boundary decreases with increasing boundary velocity, while positive η means that it increases. If η is zero or negative, we find that the steady state is always linearly stable. If η is positive, then the stability of the steady state can be obtained from the results of Kurtze, van Saarloos, and Weeks⁸ for complete explosive crystallization by replacing the wave numbers and linear growth rates of all perturbations by the rescaled values defined in Eq. (3.5) and the parameters α and β by their rescaled versions given in (3.6). The rescaling of α and β decreases the value of α and increases that of β at the stability boundary as η increases. Thus if η is increased, then some parameter values which would correspond to stable steady states for smaller η now yield unstable steady states. This can be understood by noting that two effects control the instability. First, if a fluctuation increases the boundary velocity, then the amount of latent heat being released changes, increasing if η is positive and decreasing if it is negative. In the former case this tends to raise the boundary temperature and hence increase the velocity further. On the other hand, if the boundary moves faster than it would in steady state, then it "outruns" the heat that was released at its previous positions,⁶ and so its temperature tends to decrease, lowering the velocity. For negative η these two effects cooperate and so stabilize the steady state, while for positive η they compete and can lead to oscillations. An increase in the fraction of crystallization with increasing boundary velocity (which increases η) then strengthens the first, destabilizing effect, and so makes previously stable steady states unstable. Finally, according to (3.5) the oscillation frequencies and transverse wave numbers of all perturbations decrease as η increases. This then increases the spacing between undulations left on the

surface of the film when the transition has finished.

The parameter $\alpha' = \alpha\eta$ admits a simple physical interpretation: From the definitions (3.2) and (3.3) of α and η , we see that α' is given by

$$\alpha' = (\beta^{1/2}/V^b)d[(L/c)V^bf(V^b)]/dT^b|_{ss}. \quad (4.1)$$

Thus α' measures the sensitivity of the rate of latent heat release to the *temperature* at the transition front, as η measures its sensitivity to the boundary velocity. The result that negative η stabilizes the steady state is valid only when the boundary velocity is an increasing function of temperature (α positive), so that both η and α' are negative.

The stability calculation done by Kurtze, van Saarloos, and Weeks for complete crystallization also allowed for capillary effects on the interface kinetics and for an external line source of heat⁵ to drive the boundary at a prescribed speed. These effects can also be included in the present calculation, with the same results: the new stability equation is identical to the old with the replacements (3.5) and (3.6). The additional parameters, d_0 , which measures the effect of the curvature of the boundary on its velocity, and R , which measures the importance of the laser, are unchanged [provided the factor L which appears in the definition of R is replaced by $Lf(V)$, as it is in the definition (3.2) of α]. Thus the results of the stability calculation for laser-driven growth can be transcribed to the more general case just as those for self-sustained growth can.

Van Saarloos and Weeks⁷ analyzed a codimension-2 bifurcation of the steady state which occurs at the point $\alpha=3$, $\beta=\frac{2}{3}$, obtaining the nonlinear behavior of the interface in the vicinity of this point. Kurtze¹¹ has also carried out a nonlinear analysis of the one-dimensional oscillatory instability of laser-driven growth in a regime in which self-sustained growth at the laser scan speed is almost energetically possible. Little modification is needed in order to carry these calculations over to the present problem: apart from the rescalings (3.5) and (3.6), the coefficients of the nonlinear terms in the resulting equations are merely changed by terms involving the derivatives of $f(v)$.

There are a number of other possible physical systems which could be modeled by a moving boundary problem similar to that stated in Sec. II.¹¹ For example, thermite reactions, in which the reagents are initially in intimate contact and only need an activation energy in order to react, could be described by essentially the same equations. Note that in a three-dimensional problem, in which we are interested in the stability of an advancing planar boundary, we would set the heat-loss parameter Γ in the diffusion equation (2.1) to zero (provided we can ignore losses due to radiation). According to the definition (2.4), this then makes the parameter β equal to 1. In this case the full range of behavior of the boundary is still available, the difference being that now the relevant theoretical parameters are α' and $1/\eta$ rather than α and β . We may also generalize the interpretation of our model to cover physical systems in which the relevant diffusion field is not heat, but, say, the concentration of some chemical species. An example of such a system would be the direc-

tional solidification of certain binary mixtures, in which the concentration of some impurity or chemical constituent of the solid may oscillate in a direction perpendicular to the growth direction.^{12,13} In this case the loss param-

eter Γ is indeed absent, and we must interpret LfV^b/c as the rate at which this impurity is being rejected at the transition front. These studies will be reported in a future publication.

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