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Growth from a hypercooled melt near absolute stability

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We study the stability of a solid-liquid interface in a hypercooled melt, taking into account attachment kinetics, surface energy, and surface energy in the heat balance. There is a basic-state solution with the planar interface moving at constant speed. Linear-stability theory gives a long-wave absolute-stability limit. Near this point we introduce a string model in which we use a thermal-boundary-layer approximation and obtain an evolution equation for the interface. In a limiting case this interface equation reduces to a Kuramoto-Sivashinsky equation. Comparison with experimental and numerical results are discussed and a conceptual picture of unconstrained growth for all undercoolings is addressed.

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I. INTRODUCTION

Unconstrained growth from a pure undercooled liquid has long been studied as a “simple” system displaying complex dendritic dynamics. The heat liberated on the solidification front is conducted through each phase. The local-equilibrium temperature of the front is determined by the Gibbs-Thomson effect, in which surface energy times curvature of the interface creates capillary undercooling. When the front has significant speed, there enters another factor that causes interfacial undercooling, atomic-attachment kinetics.

When the undercooling is small enough, a planar front can propagate with a time-dependent speed $V \sim t^{-1/2}$. The front is then always unstable, perhaps, leading to the formation of dendrites. When undercooling is large enough, there is a kinetics-controlled steady planar solution [1–4] in which the interface propagates at constant speed. The stability of this plane-front solution has been examined by Novick-Cohen [5], Frankel [6], and Misbah, Muller-Krumbhaar, and Temkin [7], who showed that there is a critical undercooling above which the planar state is stable. They used long-scale asymptotics to derive a Kuramoto-Sivashinsky equation in the neighborhood of this absolute-stability point.

Wollkind [8], using continuum balances on the solid-liquid interface, derived a heat-balance equation that includes the effect of surface energy. Umantsev and Roitburd [9] derived the identical condition from thermodynamical arguments. This generalized condition has to date not been incorporated into models of front dynamics.

In what follows we examine the problem, generalized by the inclusion of the surface-energy contribution, and, furthermore, take a different approach. We treat the front as a string and use a thermal-boundary-layer approximation to determine an evolutionary system for the front. In a limiting case this system reduces to the Kuramoto-Sivashinsky equation [5–7] for the front dy-

namics; away from this limiting case the string equation may contain richer dynamics. Finally, we try to give a conceptual picture of unconstrained growth valid for all undercoolings by using the present results and observations of others.

II. FORMULATION

We consider the so-called “one-sided” model of the two-dimensional case in which heat conduction is allowed only in the liquid. We do so for simplicity, but also because numerical simulations of related problems [3,10] show that heat flow into the solid is always small for the solidification of strongly supercooled liquids. Extension to the “two-sided” model is given herein.

Heat conduction in the liquid is described by

$$C \frac{\partial T}{\partial t} = \lambda \nabla^2 T, \quad \nabla^2 = \frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial Z^2}, \quad (2.1)$$

where λ and C are, respectively, the thermal conductivity and the specific heat per unit volume.

The dynamics of the interface at $Z = Z_f$ is governed by the boundary conditions. The first of these characterizes the departure of the interface from local equilibrium; it determines the relation between the normal growth speed V_n and the temperature T_f of the front

$$V_n = \mu (T_E - T_f). \quad (2.2)$$

Here μ is the kinetic coefficient and T_E is the local-equilibrium temperature, which depends upon the curvature K of the interface according to the Gibbs-Thomson equation:

$$T_E = T_m [1 - \gamma K / L]. \quad (2.3)$$

Here γ is the surface tension (surface free energy), T_m is the melting point, and L is the latent heat of transformation per unit volume.

The second boundary condition describes the balance

between the rate of heat release at the boundary and the thermal flux into the liquid [8,9]:

$$\lambda \partial_n T_l = V_n (L - \gamma K) . \quad (2.4)$$

Here ∂_n is the derivative in the direction normal to the front of solidification and pointing into the liquid. The first term on the right-hand side describes the production of latent heat, while the second one is due to the creation or destruction of the interfacial area and hence surface energy. Actually, instead of the surface free energy γ this term is proportional [9] to the surface energy ($\gamma - T d\gamma/dT$). However, the surface entropy ($-d\gamma/dT$) is usually very small and will be neglected here. The surface-energy term is the only one that contributes to a curvature-driven motion [11,12].

The problem we consider involves a pure liquid that is supercooled to temperature $T_\infty < T_m$ and solidifies with the condition

$$T \rightarrow T_\infty \text{ as } Z \rightarrow \infty . \quad (2.5)$$

When the supercooling of a liquid is large enough $T_\infty < T_m - L/C$ (hypercooled liquid), there exists [1-4] a solution with a planar interface that moves at constant speed. This behavior is represented by the basic-state solution to the system (2.1)–(2.5) as follows:

$$T(Z, t) = T_\infty + (L/C) \exp[-(V_0/\alpha)(Z - Z_f)] , \quad Z > Z_f(t) \quad (2.6)$$

$$Z_f \sim V_0 t , \quad (2.7)$$

$$V_0 = \mu(T_m - T_\infty - L/C) , \quad (2.8)$$

where the Z axis is directed towards the liquid phase perpendicular to the planar front, V_0 is its speed, and $\alpha = \lambda/C$ is the thermal diffusivity. The temperature in the solid is constant.

III. GEOMETRICAL APPROACH TO THE INTERFACE EVOLUTION

We now introduce a geometrical approach to the problem (2.1)–(2.5). In a two-dimensional space a front between solid and liquid can be represented as a string which is a heat source that moves according to the evolution of the temperature field. The geometry of the string is determined by its natural equation in which the curvature K is treated as a function of the arc length s :

$$K(s, t) = \partial_s \varphi . \quad (3.1)$$

Here φ is the angle between the normal to the front and a fixed direction, and ∂_s denotes differentiation with respect to arc length. The motion of the string is governed by the normal growth velocity V_n , as shown in Fig. 1. The equation of motion [13,14] for K is given by

$$\partial_t K + (\partial_s K) \int K V_n ds + K^2 V_n + \partial_s^2 V_n = 0 , \quad (3.2)$$

where ∂_t denotes the time derivative for constant s .

Notice that Eq. (3.2) has a shape-preserving solutions [13]: $K = K(\varphi)$, $V_n \propto \cos \varphi$. For a curvature-driven

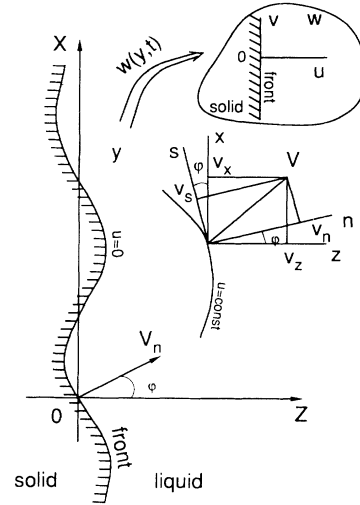


FIG. 1. The liquid-solid interface in the $y = Z + iX$ plane in the geometrical approach. V is the complex velocity of a point (u, v) , V_n is its normal, and V_s is its tangential speed. φ is the angle between the normal \mathbf{n} and the positive Z direction. Inset: the liquid-solid interface in the $w = u + iv$ plane.

motion [11] $V_n = -\beta K$ and Eq. (3.2) gives the evolution equation

$$\beta^{-1} \partial_t K = \partial_s \left[K \int K^2 ds \right] + \partial_s^2 K ,$$

which has the time-decaying solution $K(t)^{-1} = [K(0)^{-2} - 2\beta t]^{1/2}$ which describes a motion of a circle [12].

Equation (3.2) is a purely geometrical one and all dynamical features of the problem are contained in the quantity V_n . In order to relate V_n to the curvature and other quantities of our problem we analyze the thermal field utilizing a time-dependent set of orthogonal curvilinear coordinates (u, v) chosen so that $u = 0$ gives the interface position at all times. To simplify the analysis we utilize the techniques of the theory of analytic functions of complex variables.

Consider a time-dependent conformal transformation of coordinates from (Z, X) to (u, v) such that the function $w = u + iv$ is a one-to-one analytic function of $y = Z + iX$:

$$w = W(y, t) \quad (3.3)$$

with one-to-one analytic inverse function

$$y = Y(w, t) = Z(w, t) + iX(w, t) . \quad (3.4)$$

The derivative of the transform (3.4) can be written in the form

$$\frac{dy}{dw} = h e^{i\varphi} , \quad (3.5)$$

where $\varphi = \arg(y')$ is the angle between (u, v) and (Z, X) coordinates at any point (Fig. 1). Geometrical properties of coordinates (u, v) can be expressed in terms of the scale factors of the coordinates that are equal for conformal transforms:

$$h^{-2} = \left| \frac{dw}{dy} \right|^2 = \left[\frac{\partial u}{\partial Z} \right]^2 + \left[\frac{\partial u}{\partial X} \right]^2 = \left[\frac{\partial v}{\partial Z} \right]^2 + \left[\frac{\partial v}{\partial X} \right]^2. \quad (3.6)$$

Then, from the analyticity of (3.3), we obtain

$$\partial_n u = \partial_s v = h^{-1}, \quad (3.7a)$$

$$\partial_n v = \partial_s u = 0, \quad (3.7b)$$

where \mathbf{n} and \mathbf{s} are unit vectors in the directions perpendicular to the lines u is constant and v is constant, respectively (Fig. 1). For derivatives in the (Z, X) plane we have

$$\frac{\partial}{\partial Z} = (\cos\varphi)\partial_n - (\sin\varphi)\partial_s, \quad (3.8a)$$

$$\frac{\partial}{\partial X} = (\sin\varphi)\partial_n + (\cos\varphi)\partial_s, \quad (3.8b)$$

so that the Laplacian operator can be written

$$\nabla^2 = \partial_n^2 + \partial_s^2 + K\partial_n - (\partial_n\varphi)\partial_s, \quad (3.9)$$

where K is the curvature of the line $u = \text{const}$. The operators ∂_n and ∂_s do not commute. Their commutator (Poisson's brackets) can be calculated from Eqs. (3.8)

$$[\partial_s, \partial_n] = \partial_s\partial_n - \partial_n\partial_s = K\partial_s + (\partial_n\varphi)\partial_n, \quad (3.10)$$

which gives us an infinite set of formulas for the geometry of the new system of coordinates (u, v) . We shall write down some of them.

First, let us employ (3.10) on functions $u(Z, X)$ and $v(Z, X)$. Taking into account (3.7) we get

$$\partial_n h = hK, \quad (3.11a)$$

$$\partial_s h = -h\partial_n\varphi. \quad (3.11b)$$

Then, we employ form (3.10) for the argument and modulus of the function (3.5) to obtain

$$\partial_n K = -(K^2 + \partial_s^2 h / h), \quad (3.12a)$$

$$\partial_n^2 \varphi = -\partial_s K. \quad (3.12b)$$

These formulas are consequences of the fact that the argument and logarithm of the modulus of an analytic function are harmonic functions.

To characterize the dependence of the transform (3.4) on time we introduce the complex velocity of a point (u, v) in the y plane

$$\partial_t y \equiv V = V_z + iV_x, \quad (3.13)$$

where $V_z dt$ and $V_x dt$ are infinitesimal displacements of the point (u, v) in the Z and X directions after a period of time dt . Since $V(w)$ is an analytic function, we can write

$$\frac{\partial V_z}{\partial Z} = \frac{\partial V_x}{\partial X}, \quad (3.14a)$$

$$\frac{\partial V_x}{\partial Z} = -\frac{\partial V_z}{\partial X}. \quad (3.14b)$$

The differential of the function (3.3) is equal to

$$dw = \frac{\partial W}{\partial t} dt + \frac{dW}{dy} dy,$$

where $\partial/\partial t$ is the derivative in the y plane. If $dw = 0$, then from (3.5) and (3.13) we obtain

$$\frac{\partial W}{\partial t} + h^{-1} V e^{-i\varphi} = 0. \quad (3.15)$$

From the definition (3.5) of an angle φ one can see that $\text{Re}(V e^{-i\varphi})$ is the component of V in the \mathbf{n} direction. Introducing the component V_s of V in the \mathbf{s} direction we can write

$$V e^{-i\varphi} = V_n + iV_s. \quad (3.16)$$

For the transformation of coordinates this yields

$$\frac{\partial u}{\partial t} + h^{-1} V_n = 0, \quad (3.17a)$$

$$\frac{\partial v}{\partial t} + h^{-1} V_s = 0. \quad (3.17b)$$

Using the definitions (3.13) and (3.16), one can obtain

$$V_n = V_z \cos\varphi + V_x \sin\varphi, \quad (3.18a)$$

$$V_s = V_x \cos\varphi - V_z \sin\varphi. \quad (3.18b)$$

From formula (3.16) one can see that $V_n + iV_s$ is not an analytic function and from Eqs. (3.8), (3.13), (3.14), and (3.18) produce a system of equations

$$\partial_n V_n - \partial_s V_s = V_s \partial_n \varphi + V_n \partial_s \varphi, \quad (3.19a)$$

$$\partial_s V_n + \partial_n V_s = V_s \partial_s \varphi - V_n \partial_n \varphi. \quad (3.19b)$$

To proceed with our task we reformulate the problem (2.1)–(2.5) for the function $\Psi(u, v, t) = C[T(Z, X, t) - T_\infty]/L$. Utilizing (3.17), we can write for the time derivative in the y plane

$$\frac{\partial \Psi}{\partial t} = -V_n \partial_n \Psi - V_s \partial_s \Psi + \partial_t \Psi. \quad (3.20)$$

Thus forms (2.1), (3.9), and (3.20) give us the heat equation in the time-dependent curvilinear system of coordinates:

$$\left[\partial_n^2 + \left[K + \frac{V_n}{\alpha} \right] \partial_n + \partial_s^2 + \left[\frac{V_s}{\alpha} - \partial_n \varphi \right] \partial_s - \frac{1}{\alpha} \partial_t \right] \Psi = 0. \quad (3.21)$$

We must provide it with the boundary conditions (2.2)–(2.4) on the interface $u = 0$:

$$\partial_n \Psi = -(V_n / \alpha)(1 - Q l_c K), \quad (3.22)$$

$$\Psi = 1 + \theta - l_c K - l_\mu V_n / \alpha. \quad (3.23)$$

Here $l_c = CT_m \gamma / L^2$ is the capillary length, $l_\mu = \lambda / \mu L$ is the kinetic length, $\theta = (C/L)(T_m - T_\infty) - 1$ is the hypercooling of a liquid, and $Q = L / CT_m$.

This is a regular boundary-value problem, (3.21)–(3.23),

but not a free-boundary problem. It has the plane, steady solution

$$\begin{aligned} K=0, \quad \varphi=0, \quad h=\alpha/V_n, \quad V_s=0, \\ V_n=V_0=\alpha\theta/l_\mu, \quad \Psi=e^{-u}, \end{aligned} \quad (3.24)$$

which is identical to forms (2.6)–(2.8). For an arbitrary interface [15] we may choose coordinates (u, v) so that everywhere on the half-plane $u > 0$ the temperature field is given by

$$\Psi=\psi e^{-u}, \quad \psi=1-l_c K+\theta-l_\mu V_n/\alpha \quad (3.25)$$

and

$$\partial_n \Psi = -(V_n/\alpha)(1-Ql_c K)e^{-u}. \quad (3.26)$$

For the scale factor h this yields

$$h = \frac{1-l_c K+\theta-l_\mu V_n/\alpha}{(V_n/\alpha)(1-Ql_c K)-l_c \partial_n K-l_\mu \partial_n V_n/\alpha}. \quad (3.27)$$

We then multiply Eq. (3.21) by h and take the line integral along the line $v = \text{const}$ from $u = 0$ to ∞ , taking into account relations (3.22), (3.23), and (3.25)–(3.27), to get the heat equation in the integral form:

$$\begin{aligned} & \left\{ \frac{V_{\hat{n}}}{\alpha} \left[\frac{l_\mu V_{\hat{n}}}{\alpha} - \theta \right] \right. \\ & \left. + \left[\left[\frac{l_\mu V_{\hat{n}}}{\alpha} - \theta \right] + \left[\frac{l_c V_{\hat{n}}}{\alpha} - 1 \right] \right] K + l_c K^2 \right\}_{u=0} \\ & = \int_0^\infty \left[\partial_{\hat{n}} K + \frac{1}{\alpha} \partial_{\hat{n}} V_{\hat{n}} - \partial_{\hat{s}}^2 + \left[\partial_{\hat{n}} \varphi - \frac{1}{\alpha} V_{\hat{s}} \right] \partial_{\hat{s}} \right. \\ & \quad \left. + \frac{1}{\alpha} \partial_t \right] \psi h e^{-u} du. \end{aligned} \quad (3.28)$$

From Eq. (3.28) one can then obtain the first approximation to the basic state (3.24):

$$\frac{V_n}{\alpha} = \frac{\theta}{l_\mu} + \frac{1-\theta(1-Q)R^{-1}}{\theta} K + o(K), \quad R = \frac{l_\mu}{l_c} \quad (3.29)$$

which shows that all perturbations of a plane front grow if $\theta < R/(1-Q)$ and decay if $\theta > R/(1-Q)$ [16]. Thus the absolute stability criterion can be expressed as

$$\theta_c = R/(1-Q). \quad (3.30)$$

The absolute stability boundary is approached when the thermal length $l_T = \alpha/V_n$ becomes equal to $l_c(1-Q)$. If $Q=0$ this criterion of linear stability coincides with the criterion [5–7], which has been obtained by the normal-mode analysis, but without the consideration of the dissipation mechanism in (2.4).

Now we want to introduce the thermal boundary-layer model for the nonlinear analysis of Eq. (3.28). Functions $\psi(u, v, t)$ and $h(u, v, t)$ do not vary strongly in this layer as compared with $\exp(-u)$ because the thickness of this layer l_T is much smaller than its radius of curvature (large-Péclet-number approximation). Thus the term before the exponent can be removed from the integral and

we can write down the equation for the interface $u = 0$:

$$\begin{aligned} & \frac{V_n}{\alpha} \left[\frac{l_\mu V_n}{\alpha} - \theta \right] + \left[\left[\frac{l_\mu V_n}{\alpha} - \theta \right] + \left[\frac{l_c V_n}{\alpha} - 1 \right] \right] K \\ & + (l_c + \psi h) K^2 + \psi \partial_s^2 h + h \partial_s^2 \psi + (\partial_s h)(\partial_s \psi) \\ & + \frac{1}{\alpha} h (V_s \partial_s \psi - \psi \partial_n V_n) - \frac{1}{\alpha} h \partial_t \psi = 0. \end{aligned} \quad (3.31)$$

The set of equations (3.19), (3.27), and (3.31) determines the relation between V_n , K , and φ on the interface $u = 0$ in the limit of a thin thermal layer, and constitutes a closed system for the evolution of the front.

To examine the nonlinear development of the unstable long waves near the absolute stability limit we introduce the small parameter ϵ which measures departures from the absolute stability boundary:

$$\epsilon = 1 - \theta \frac{1-Q}{R}. \quad (3.32)$$

Then Eqs. (3.2) and (3.29) give us the scaling of these waves:

$$\frac{1}{t} \sim \frac{\epsilon}{s^2} \sim K. \quad (3.33)$$

The set of equations (3.19), (3.27), and (3.31) admits the solution, consistent with this scaling:

$$\psi = 1 - l_c K + O(\epsilon^3), \quad (3.34a)$$

$$h = \frac{l_\mu}{\theta} [1 - (1-Q)l_c K] + O(\epsilon^3), \quad (3.34b)$$

$$\frac{V_s}{\alpha} = -\frac{\theta}{l_\mu} \varphi + O(\epsilon^{5/2}), \quad (3.34c)$$

$$\frac{V_n}{\alpha} = \frac{\theta}{l_\mu} + \frac{\epsilon}{\theta} K + (2-Q) \frac{l_c l_\mu}{\theta^2} \partial_s^2 K + O(\epsilon^4), \quad (3.34d)$$

$$s \sim \epsilon^{-1/2}, \quad t \sim \epsilon^{-2}, \quad \varphi \sim \epsilon^{3/2}, \quad K \sim \epsilon^2. \quad (3.34e)$$

If we insert the expression for V_n , given by (3.34d) into Eq. (3.2), we obtain the *evolution equation of the front in its natural coordinates*

$$\frac{1}{\alpha} \partial_t K + \frac{\theta}{2l_\mu} \partial_s^2 \left[\int K ds \right]^2 + \frac{\epsilon}{\theta} \partial_s^2 K + (2-Q) \frac{l_c l_\mu}{\theta^2} \partial_s^4 K = 0. \quad (3.35)$$

To write this equation in Cartesian coordinates we denote the interface position in the frame of reference moving with the speed V_0 as $Z_f = H(X, t)$ and recall that $s \simeq X$ and $K \simeq -H_{XX}$. Then Eq. (3.35) is as follows [17]:

$$\begin{aligned} & (1/\alpha) H_t + (2-Q)(l_c l_\mu / \theta^2) H_{XXXX} \\ & + (\epsilon/\theta) H_{XX} - (\theta/2l_\mu) H_X^2 = 0. \end{aligned} \quad (3.36)$$

The mean relative velocity of the front can be determined as

$$\langle V_r \rangle \equiv \frac{1}{t} \int_0^t \frac{1}{X_0} \int_0^{X_0} H_t dX dt, \quad (3.37)$$

where X_0 is the size of a crystal in X direction. We can rescale Eq. (3.36) with

$$x = \left[\frac{4|\epsilon|/\Lambda}{(1-Q)(2-Q)} \right]^{1/2} \frac{X}{l_c}, \quad \tau = \frac{4}{2-Q} \left[\frac{\epsilon}{\Lambda} \right]^2 \frac{\alpha t}{l_\mu l_c},$$

$$\xi = -\frac{1}{1-Q} \frac{\theta}{\epsilon} \frac{H}{l_c}, \quad \Lambda = \frac{\epsilon}{(1-Q)(2-Q)} \left[\frac{X_0}{\pi l_c} \right]^2 \quad (3.38)$$

to obtain the normalized Kuramoto-Sivashinsky equation on the interval $0 \leq x \leq 2\pi$,

$$\xi_\tau + 4\xi_{xxxx} + \Lambda q (\xi_{xx} + \frac{1}{2}\xi_x^2) = 0, \quad (3.39)$$

where $q = \text{sgn}\epsilon$. This is an evolution equation of the Kuramoto-Sivashinsky type that governs the stability of the basic state $\xi=0$. For $Q=0$ in Λ , it coincides with that given by Novick-Cohen [5] in the zero-temperature-gradient limit, Frankel [6], and Misbah, Müller-Krumbhaar, and Temkin [7]. Much work (see, e.g., [18,19]) has been done on the spatiotemporal dynamics of this equation. For $q=1$, the planar state is linearly unstable if $0 < k^2 < (4\Lambda)^{-1}$ and stable otherwise. For $q=-1$, the planar state is linearly stable. For the 2π -periodic solutions of (3.39) we can obtain an expression for the mean relative velocity

$$\langle V_r \rangle = 2 \frac{(1-Q)^3}{2-Q} \frac{V_0}{R^2} \epsilon^3 \frac{\langle \xi_x^2 \rangle}{\Lambda},$$

$$\langle \xi_x^2 \rangle = \frac{1}{2\pi\tau_0} \int_0^{\tau_0} \int_0^{2\pi} \xi_x^2 dx d\tau.$$

Hyman and Nicolaenko [18] have shown that $\langle \xi_x^2 \rangle$ is proportional to Λ . Thus $\langle V_r \rangle$ is independent of Λ , the size of the growing crystal. Hence the mean speed of a growing crystal in the laboratory frame of reference can

be written as follows:

$$V = V_0 \left[1 + b \frac{\epsilon^3}{R^2} \right], \quad (3.40)$$

with numerical coefficient $b \approx 1$. This equation gives the local transcritical bifurcation structure from the planar front to a cellular interface near the point of absolute stability. From Eq. (3.25), (3.27), (3.34a), and (3.34b) we can retrieve the temperature field for hypercoolings $\theta < R/(1-Q)$ and see that the first correction to the temperature field of the basic state is of the order ϵ^3 and comes from the surface tension of the curved front. Finally, from the scaling (3.34e) and (3.38) one can see that near the absolute stability $|H| \ll l_T \ll K^{-1}$. It means that we have thin thermal boundary layer ($Kl_T \ll 1$, large Péclet number) in front of a slightly deflected interface ($|H| \ll l_T, |\varphi| \ll 1$).

From Eq. (3.2) it can be seen that an evolution of any front should always obey an equation of the Kuromoto-Sivashinsky type if the normal component of its growth rate relates to its curvature as

$$V = C_1 + C_2 K + C_3 \partial_s^2 K + O(K), \quad (3.41)$$

where the C_i are constants. This can be true near the absolute-stability limit. Thus the same or related equations appear in many problems of widely varying physical nature [20].

IV. DISCUSSION OF EXPERIMENTS

The critical value of the hypercooling $\theta_c = R/(1-Q)$ is the only point of the absolute stability. The parameter R is the ratio of kinetic and capillary lengths. Crystallization (as well as other phase transitions) is a process of or-

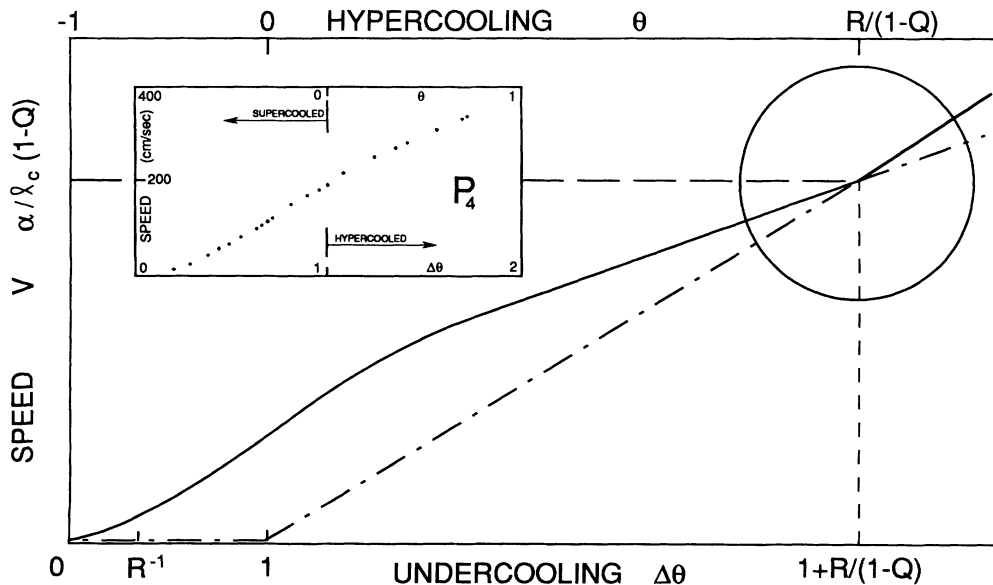


FIG. 2. Sketch of solutions V vs $\Delta\theta$ of the unconstrained growth problem. The solid line is a conjectured dendritic-cellular branch, and the dash-dotted line is the unstable planar solution. Inside the circle the Kuromoto-Sivashinsky equation applies. Inset: experimental data [2].

dering which may be described by the relaxation equation of the diffusion type. There it can be shown [21] that the parameter R is the ratio of diffusivities of two processes in the system: thermal and ordering. A typical value of the coefficients R and Q are, respectively, 100 and 0.3 for metals and 10 and 0.08 for organic liquids and white phosphorus. Thus, to reach the absolute stability boundary one needs to hypercool the liquid strongly below the melting point. However, the temperature of a liquid should not fall below the limit of the thermodynamic stability of a liquid state. Besides, the capillary length l_c should be much larger than the thickness of the interfacial transition region. Otherwise, when $l_T \leq l_c$, the boundary conditions (2.2)–(2.4) are no longer valid and the concept of the front ceases to be meaningful. Both restrictions can be fulfilled for substances with low values of the parameter Q [21].

The restoration of stability during solidification of hypercooled liquids has been experimentally observed in the crystallization of cyclohexanol, which has $Q=0.03$. Ovsienko, Alifintsev, and Maslov [22] have remarked that rounded, macroscopically smooth forms appear at large supercoolings of the sample. The appearance of crystals with morphologically smooth fronts from hypercooled liquid has been seen in computer simulations of dendritic growth [10] and was attributed to a decrease of the thermal length. However, the point of the absolute stability was thought to occur when the thermal length is equal to the radius of curvature of the tip of a dendrite; Eq. (3.30) gives the correct result, $l_T=(1-Q)l_c$.

The derived theory, together with experimental and numerical results [2,10,22,23], may aid in giving one a conceptual picture of unconstrained growth over the full range of undercoolings $\Delta\theta=1+\theta$.

In Fig. 2 we plot mean front speed versus undercooling. The dash-dotted curve represents the planar front, traveling at $t^{1/2}$ for $\Delta\theta < 1$ and at constant speed for $\Delta\theta > 1$. The planar interface is always unstable for $0 < \Delta\theta < 1+R/(1-Q)$, but is stabilized at $\Delta\theta_c$, the absolute stability boundary. The solid curve in Fig. 2 represents our conjecture for the curve of the dendritic-cellular branch that emerges from the unstable plane solution. For small supercoolings $\Delta\theta$ there is a quasiequilibrium region where surface-energy effects dominate ($\Delta\theta < R^{-1}$). For larger undercoolings ($\Delta\theta > R^{-1}$), kinetic effects are more important.

In the inset of Fig. 2 the experimental data of Glicksman and Schaefer [2] on white phosphorous, display two points of inflection near $\Delta\theta=1$ which may suggest the existence of morphological transitions. (Note that these are not evident in the log-log plot of Ref. [2].) Glicksman and Schaefer observe there a change in the morphology to a “quasiplanar” front. Furthermore, Fedorov, Borisov, and Maslov [23] show that for the succinonitrile-salol mixture there is a transition of morphologies just below the solidus, a position analogous to $\Delta\theta$ just above unity.

Our contribution applies for large $\Delta\theta$, in a neighborhood of $\Delta\theta_c$, as indicated by the circle in Fig. 2. The Kuromoto-Sivashinsky equation (3.36) governs, among other things, the bifurcation to cells whose mean speeds

are given by Eq. (3.40). The string theory applies here as well, but may have broader validity. Our conjecture is that our local solutions near $\Delta\theta_c$ are part of the single branch shown in Fig. 2 along which several points of transition occur.

V. CONCLUSIONS

We have considered a pure liquid solidifying due to deep supercooling. When the supercooling $\Delta\theta$ exceeds unity, a planar interface can propagate at constant speed. A string theory is employed in which the evolution of the string curvature K is related to its normal speed V_n .

For $\Delta\theta > 1$ the linear stability theory of the planar front shows that the front is unstable for all $\Delta\theta$ up to the critical value $\Delta\theta_c=1+R/(1-Q)$ at which point the front is restabilized by the joint effects of surface energy and kinetic undercooling. This result generalizes that of [5–7] to include surface energy in the interfacial-heat-flux condition ($Q \neq 0$). Using typical values, $Q \approx 0.30$ for metals and 0.08 for organic liquids and white phosphorous, one can see that in the former case, there is a significant shift in the absolute-stability boundary by the inclusion of these surface-energy effects. For phase transitions different from solidification the parameter Q may be even larger than unity which shifts the point of absolute stability substantially to the region of supercoolings $\Delta\theta < 1$. This might be the reason for the stability of interfaces in many solid-state diffusional transformations from a metastable phase.

Furthermore, the string theory used yields the linear stability boundary without the necessity of introducing normal modes. Our approach relies on the approximation of the thin thermal-boundary layer (large Péclet number) in front of a slightly deflected interface ($|\varphi| \ll 1$) which is justified near the absolute stability boundary. This yields the relation $V_n=V_n(K)$, Eq. (3.34d), that governs the interface dynamics. This form is familiar from the work of Brower *et al.* [13], who *assumed* such a law in their examination of dendrite dynamics in the absence of kinetic effects. In our case we have *derived* such a relation and it holds only near the absolute-stability boundary. If form (3.41) is used in (3.2), then we obtain the Kuromoto-Sivashinsky equation for the interface evolution. One advantage of the string theory as compared to the singular asymptotic method [5–7] is that it *may* have the potential of describing behavior farther from the absolute-stability boundary.

The local bifurcation structure of mean speed V versus undercooling $\Delta\theta$, as given by the string theory, can be incorporated into a conceptual picture of unconstrained growth for all $\Delta\theta$, as discussed in Sec. VI.

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