Lawrence Berkeley National Laboratory

Recent Work

Title

ON CELLULAR INSTABILITY IN THE SOLIDIFICATION OF A DILUTE BINARY ALLOY

Permalink

<https://escholarship.org/uc/item/62r5m5jq>

Author

Sivashinsky, G.I.

Publication Date

1982-06-01

Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

Physics, Computer Science & Mathematics Division

RECEIVED
LAWRENCE
BERKELEY LABORATORY

SEP 30 1982

To be submitted for publication

LIBRARY AND
DOCUMENTS SECTION

ON CELLULAR INSTABILITY IN THE SOLIDIFICATION
OF A DILUTE BINARY ALLOY

G.I. Sivashinsky

June 1982

TWO-WEEK LOAN COPY

*This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 6782.*

LBL-14764
c.2

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

**ON CELLULAR INSTABILITY
IN THE SOLIDIFICATION OF A DILUTE BINARY ALLOY¹**

G.I. Sivashinsky²

Department of Mathematics and Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

June 1982

¹Supported in part by the Director, Office of Energy Research, Office of Basic Energy Sciences, Engineering, Mathematical, and Geosciences Division of the U.S. Department of Energy under contract DE-AC03-76SF00098.

²On leave from the Department of Mathematical Sciences, Tel-Aviv University, Ramat-Aviv, Tel-Aviv 69978, Israel.

ON CELLULAR INSTABILITY IN THE SOLIDIFICATION OF A DILUTE BINARY ALLOY³

G.I. Sivashinsky⁴

Department of Mathematics and Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

July 1982

Abstract

In the solidification of a dilute binary alloy, a planar solid-liquid interface is often found to be unstable, spontaneously assuming a cellular structure. If the solute rejection coefficient is close to unity, then, near the stability threshold, the characteristic cell size may significantly exceed the diffusional width of the solidification zone. This situation enables one to derive an asymptotic nonlinear equation which directly describes the dynamics of the onset and stabilization of cellular structure:

$$f_{\tau} + \nabla^4 f + \nabla[(2-f)\nabla f] + \alpha f = 0.$$

³Supported in part by the Director, Office of Energy Research, Office of Basic Energy Sciences, Engineering, Mathematical, and Geosciences Division of the U.S. Department of Energy under contract DE-AC03-76SF00098.

⁴On leave from the Department of Mathematical Sciences, Tel-Aviv University, Tel-Aviv 69978, Israel.

1. Introduction

Problems of linear stability in the physics of continuous media frequently lead to dispersion relations expressible as equations of the type

$$\omega = (R - R_c)k^2 - k^4, \quad k = |\vec{k}| \quad (1)$$

near the stability threshold (R_c); here ω and $\vec{k}$ are the growth rate and wave vector of a small harmonic perturbation:

$$\Phi \sim \exp(\omega t + i\vec{k} \cdot \vec{x}). \quad (2)$$

Φ is a certain characteristic function, whose precise meaning depends on the problem context. Comparing (1) and (2), we obtain the following equation for the linear evolution of Φ :

$$\Phi_t + (R - R_c)\nabla^2\Phi + \nabla^4\Phi = 0. \quad (3)$$

At $R > R_c$, Eq. (3) implies exponential amplification of long-wave perturbations. In real situations, this unrestricted amplification of the perturbation is usually suppressed by nonlinear effects, which may correspond to certain nonlinear terms not appearing in Eq. (3):

$$\Phi_t + (R - R_c)\nabla^2\Phi + \nabla^4\Phi + \text{nonlinear terms} = 0. \quad (4)$$

The spatial dimensionality of the characteristic function Φ is often less than that of the initial problem. Hence, the construction of the closed nonlinear equation (4) is an essential simplification of the problem. Indeed, a dimensionality-lowering procedure of this kind frequently proves technically possible because, by (1), near the stability threshold we have

$$k \sim \sqrt{R - R_c}, \quad \omega \sim (R - R_c)^2 \quad (5)$$

i.e., we are dealing with a process which varies slowly both in time and in space.

The approach just described has recently found successful application in deriving equations for the nonlinear evolution of phase in certain biochemical oscillations [1,2], for propagating flame fronts [3], for the free surface of a liquid film [4], and for the plane form in Bénard-Marangoni convection [5,6]. Some of these equations were even rich enough to describe chaotic behavior in the relevant physical systems.

The asymptotic technique⁵ developed in the above-cited papers has also proved effective in deriving an equation for the nonlinear evaluation of solid-liquid interfaces in crystal growth problems.

It is known (see, e.g., Langer [8]) that, under certain conditions, when a dilute binary alloy is solidifying, a planar solid-liquid interface is found to be unstable, spontaneously assuming a cellular structure. The characteristic cell size may significantly exceed the diffusional width of the solidification zone. It will be shown below that this effect becomes more prominent, near the stability threshold, as the so-called solute rejection coefficient $1-K$ comes closer to unity. Thus, structure of the interface may be not only quasi-stationary but even quasi-planar. Thanks to this, one can lower the dimensionality of the relevant mathematical problem and obtain an explicit nonlinear equation which directly describes the dynamics of the onset and crystallization of the cellular structure.

⁵The techniques employed resemble those of Newell and Whitehead [7], who studied pockets of closely related modes in Rayleigh-Bénard convection and obtained envelope equations for slow modulation. The difference is that, whereas Newell and Whitehead perturb about a finite wave number, in our case one has to perturb about zero (see (5)).

2. Mathematical Model

We start with a mathematical model originated by Mullins and Sekerka [9] to describe an experimental situation in which solidification is controlled so that the mean position of the interface ($z = 0$) moves at a constant speed V (Fig. 1). Following Wollkind and Segel [10], we assume that the thermal diffusivity D_T of the system is significantly greater than the diffusivity D of the solute. Then, if the latent heat is not too large, the heat generated on the interface may be neglected. Moreover, following Langer [8], we assume that the thermal diffusivities of the liquid and solid phases are equal. Under these simplifying assumptions, disturbances of the interface does not induce disturbance of the temperature field, which may be assumed fixed and equal to

$$T = T_0 + Gz . \quad (6)$$

Here z is the coordinate of the mean position of the interface (Fig. 1), T_0 the temperature corresponding to the undisturbed planar interface and G the imposed temperature gradient.

The diffusion of the solute in the liquid phase is described by an equation

$$C_t = VC_z + D\nabla^2 C , \quad z \geq \Phi(x, t) \quad (7)$$

where C is the concentration of the solute, $z = \Phi$ the equation of the liquid-solid interface.

The temperature at the interface depends both on the curvature of the interface ν and on the solute concentration C ; on the assumption that C is small:

$$T = T_m(0) + (dT_m(0)/dC)C - T_m(0)\Gamma\nu \quad (z = \Phi) . \quad (8)$$

Here $T_m = T_m(C)$ is the equilibrium melting temperature of the planar interface. $C = 0$ corresponds to the pure solvent. Γ is the capillarity constant,

$$\nu = - \frac{\Phi_{xx}}{(1 + \Phi_x^2)^{3/2}}. \quad (9)$$

It follows from (6) and (8) that

$$T_0 = T_m(0) + (dT_m(0)/dC)C_0 \quad (10)$$

where C_0 is the solute concentration at the planar interface.

Eliminating the temperature from (6) and (8), we obtain the following direct relationship between the solute concentration at the interface and its geometry:

$$C = C_0 + \frac{T_m(0)\Gamma\nu + G\Phi}{dT_m(0)/dC}. \quad (11)$$

Conservation of the solute at the interface yields the equation

$$V_n(K-1)C = D \frac{dC}{dn} \quad (12)$$

where

$$\vec{n} = \frac{(-\Phi_x, 1)}{\sqrt{1 + \Phi_x^2}}$$

is the unit vector normal to the interface and

$$V_n = \frac{(V + \Phi_t)}{\sqrt{1 + \Phi_x^2}}$$

is the normal speed at which the interface is moving. K is the distribution coefficient, defined as the ratio of the equilibrium concentration of solute on the solid side of the interface to that on the liquid side ($K < 1$).

Thus,

$$C \rightarrow KC_0 \quad \text{as} \quad z \rightarrow \infty. \quad (13)$$

Eq. (7), together with conditions (11)-(13), fully define the mathematical problem for the unknown functions C and Φ .

The basic solution, corresponding to the undisturbed planar interface ($\Phi \equiv 0$), is

$$C^{(b)} = KC_0 + (1-K)C_0 \exp(-Vz/D) , \quad z \geq 0 . \quad (14)$$

3. Linear Stability Analysis

We first transform to nondimensional variables and parameters:

$$\begin{aligned} Vz/D &= \tilde{z} , \quad Vx/D = \tilde{x} , \quad V^2 t/D = \tilde{t} , \\ D\nu/V &= \tilde{\nu} , \quad C/C_0 = \tilde{C} , \quad V\Phi/D = \tilde{\Phi} , \\ \frac{GD}{VC_0(dT_m(0)/dC)} &= W(K-1) , \quad \frac{\Gamma VT_m(0)}{DC_0(dT_m(0)/dC)} = \beta(K-1) . \end{aligned} \quad (15)$$

In terms of these variables, problem (11)-(13) becomes

$$\begin{aligned} \tilde{C}_{\tilde{t}} &= \tilde{C}_{\tilde{z}} + \nabla^2 \tilde{C} , \quad \tilde{z} \geq \tilde{\Phi} , \\ \tilde{C} &= 1 + \beta(K-1)\tilde{\nu} + W(K-1)\tilde{\Phi} , \quad (1-K)(1+\tilde{\Phi}_{\tilde{t}})\tilde{C} + \tilde{C}_{\tilde{z}} - \tilde{\Phi}_{\tilde{z}}\tilde{C}_{\tilde{z}} = 0 , \quad \tilde{z} = \tilde{\Phi} ; \\ \tilde{C} &\rightarrow K \quad \text{as} \quad \tilde{z} \rightarrow \infty . \end{aligned} \quad (16)$$

$$\tilde{C}^{(b)} = K + (1-K)\exp(-\tilde{z}) . \quad (17)$$

Linear analysis of the stability of the basic solution (17) yields the following dispersion relation (Wollkind and Segel [10]):

$$\begin{aligned} \omega &= (1 - W - \beta k^2) \left[\sqrt{1/4 + k^2 + \omega} + K - 1/2 \right] - K \\ &(\tilde{\Phi} \sim \exp(\omega \tilde{t} + ik\tilde{x})) . \end{aligned} \quad (18)$$

Fig. 2 exhibits the position of the neutral stability curves for various values of K . At small $W_c - W$ ($W_c = 1$), in the instability region:

$$k \sim \sqrt{W_c - W} , \quad \omega \sim K \sim (W_c - W)^2 . \quad (19)$$

Thus, the disturbed structure of the interface turns out here to be both quasi-stationary and quasi-one-dimensional. For such values of the parameters, the

dispersion relation (18) simplifies to

$$\omega \simeq (W_c - W)k^2 - \beta k^4 - K \quad (W_c = 1). \quad (20)$$

This expression highlights the role of each of the parameters (Fig. 3). At $W < W_c$, instability sets in only at sufficiently small values of the distribution coefficient K .

4. Nonlinear Asymptotic Analysis

For the sequel, it is convenient to transform to a curvilinear coordinate system attached to the disturbed interface:

$$\tilde{z} - \tilde{\Phi}(\tilde{x}, \tilde{t}) \rightarrow \tilde{z}, \quad \tilde{x} \rightarrow \tilde{x}, \quad \tilde{t} \rightarrow \tilde{t}. \quad (21)$$

Problem (16) then becomes

$$\begin{aligned} \tilde{C}_t &= (1 + \tilde{\Phi}_t) \tilde{C}_z + \tilde{C}_{zz} + (1 + \tilde{\Phi}_z^2) \tilde{C}_{zz} - 2\tilde{\Phi}_z \tilde{C}_{zz} - \tilde{\Phi}_{zz} \tilde{C}_z, \\ (1 - K)(1 + \tilde{\Phi}_t) \tilde{C}(0) + (1 + \tilde{\Phi}_z^2) \tilde{C}_z(0) - \tilde{\Phi}_z \tilde{C}_{zz}(0) &= 0, \\ \tilde{C}(0) &= 1 + \beta(1 - K) \tilde{\Phi}_{zz} - (1 - K) W \tilde{\Phi}, \quad \tilde{C}(\infty) = K. \end{aligned} \quad (22)$$

We put

$$W = W_c(1 - \varepsilon) \quad (\varepsilon \ll 1). \quad (23)$$

Our previous estimates (19) now suggest the following definitions of scaled variables and parameters:

$$\xi = \tilde{x} \sqrt{\varepsilon}, \quad \zeta = \tilde{z}, \quad \tau = \varepsilon^2 \tilde{t}, \quad K = \kappa \varepsilon^2. \quad (24)$$

In terms of these variables, we shall look for a solution of problem (22) in the form

$$C = \kappa \varepsilon^2 + (1 - \kappa \varepsilon^2) \exp(-\zeta) + \varepsilon u(\xi, \zeta, \tau, \varepsilon),$$

$$u = u^0 + \varepsilon u^1 + \varepsilon^2 u^2 + \dots$$

$$\mathfrak{F} = \varepsilon F(\xi, \tau, \varepsilon) = \varepsilon(F^0 + \varepsilon F^1 + \varepsilon^2 + \dots) . \quad (25)$$

The problem in the zeroth approximation is

$$\begin{aligned} u_\xi^0 + u_{\xi\xi}^0 &= 0 , \\ u^0(0) + u_\xi^0(0) &= 0 , \quad u^0(0) + W_c F^0 = 0 , \quad u^0(\infty) = 0 . \end{aligned} \quad (26)$$

Hence

$$u^0 = -W_c F^0 \exp(-\xi) . \quad (27)$$

As this stage the zeroth approximation is defined only up to an as yet unknown factor $W_c F^0$. To determine this factor, we proceed to the next (first) approximation.

$$\begin{aligned} u_\xi^1 + u_{\xi\xi}^1 &= -u_{\xi\xi}^0 - F_{\xi\xi}^0 \exp(-\xi) , \\ u^1(0) + u_\xi^1(0) &= 0 , \quad u^1(0) + W_c F^1 = \beta F_{\xi\xi}^0 + W_c F^0 , \quad u^1(\infty) = 0 . \end{aligned} \quad (28)$$

The solution is

$$u^1 = (-W_c F^1 + W_c F^0 + \beta F_{\xi\xi}^0) \exp(-\xi) + (1 - W_c) F_{\xi\xi}^0 \xi \exp(-\xi) - (1 - W_c) F_{\xi\xi}^0 . \quad (29)$$

From boundary condition at $\xi = \infty$

$$(1 - W_c) F_{\xi\xi}^0 = 0 \quad \text{or} \quad W_c = 1 . \quad (30)$$

Thus, although we have obtained a numerical value for W_c , the function F^0 is still undefined. We therefore go on to the second approximation:

$$\begin{aligned} u_\xi^2 + u_{\xi\xi}^2 &= -u_{\xi\xi}^1 - F_{\xi\xi}^1 \exp(-\xi) + u_\tau^0 + F_\tau^0 \exp(-\xi) - \\ &\quad - (F_\xi^0)^2 \exp(-\xi) + 2F_\xi^0 u_{\xi\xi}^0 + F_{\xi\xi}^0 u_\tau^0 , \end{aligned} \quad (31)$$

$$\begin{aligned} u^2(0) + u_\tau^2(0) &= \kappa u^0(0) - F_\tau^0 + (F_\xi^0)^2 + F_{\xi\xi}^0 u_\xi^0(0) , \\ u^2(0) + W_c F^2 &= \beta F_{\xi\xi}^1 + W_c F^1 + \kappa W_c F^0 , \quad u^2(\infty) = 0 . \end{aligned} \quad (32)$$

The solution is

$$\begin{aligned}
u^2 = & [-F^2 + F^1 + \beta F_{\xi\xi}^1 + 2\kappa F^0 + F_{\xi\xi}^0 + \beta F_{\xi\xi\xi\xi}^0 - (F_{\xi}^0)^2 - F^0 F_{\xi\xi}^0] \exp(-\zeta) + \\
& + [\beta F_{\xi\xi\xi\xi}^0 + F_{\xi\xi}^0 - (F_{\xi}^0)^2 - F^0 F_{\xi\xi}^0] \zeta \exp(-\zeta) - \\
& F_{\tau}^0 - \kappa F^0 - F_{\xi\xi}^0 - \beta F_{\xi\xi\xi\xi}^0 + (F_{\xi}^0)^2 + F^0 F_{\xi\xi}^0 .
\end{aligned} \tag{33}$$

Condition at $\xi = \infty$ yields the desired equation for F^0 :

$$F_{\tau}^0 + \beta F_{\xi\xi\xi\xi}^0 + [(1-F^0)F_{\xi}^0]_{\xi} + \kappa F^0 = 0 . \tag{34}$$

Via the transformation

$$F^0 = (1/2)f , \quad \tau = 4\beta\bar{\tau} , \quad \xi = \sqrt{2\beta}\bar{\xi} , \quad \kappa = (1/4\beta)\alpha \tag{35}$$

Eq. (34) can be brought to the following one-parameter form, which is more convenient for analysis:

$$f_{\bar{\tau}} + f_{\bar{\xi}\bar{\xi}\bar{\xi}\bar{\xi}} + [(2-f)f_{\bar{\xi}}]_{\bar{\xi}} + \alpha f = 0 . \tag{36}$$

Considerations of symmetry and invariance show that, in the three-dimensional case, the equation for $f = f(\bar{\xi}, \bar{\eta}, \bar{\tau})$ must have the form

$$f_{\bar{\tau}} + \nabla^4 f + \nabla[(2-f)\nabla f] + \alpha f = 0 . \tag{37}$$

5. Some Basic Properties of Equation (36)

The structure of Eq. (36) immediately yields certain qualitative conclusions about the evolution of the disturbances. First, it is clear that, since $\alpha > 0$, the mean position of the interface always returns to its undisturbed state. Thus, it suffices to consider the case in which, through the entire time interval,

$$\int_{-\infty}^{\infty} f(\bar{\xi}, \bar{\tau}) d\bar{\xi} = 0 . \tag{38}$$

The initial amplification of small disturbances is due to the positive sign of $2-f$. On sections of the interface where f is positive, the instability will become weaker as the amplitude increases. Wherever f is negative, however, the instability will become stronger. This is apparently the explanation for the

characteristic profile of the experimentally observed solidification front: the sections of the front convex toward higher temperatures have considerably lower curvature than those convex toward lower temperatures (Fig. 1).

It is interesting that Eq. (36) is a limiting case of the equation

$$f_{\tau} + f_{\xi\xi\xi} + [(2 - \gamma f + f^2)f_{\xi}]_{\xi} + \alpha f = 0 \quad (39)$$

which describes the evolution of a plane form of the Rayleigh-Bénard convection in nearly insulated liquid layer [11]. Parameter γ is proportional to $d\mu/dT$, where $\mu = \mu(T)$ is the temperature dependent viscosity of the liquid. Eq. (39) reduces to Eq. (36) for $\gamma \gg 1$.

Fig. 4 shows the results of numerical solution of the initial-value problem for Eq. (39) with $\alpha = 1.01$ and $\gamma = 5$ [11]. The equation was solved in the interval $0 \leq \xi \leq 11\pi$ with periodic boundary conditions. The initial condition assumed was the antisymmetric perturbation $f(0, \xi) = (\xi - 15)\exp[-(\xi - 15)^2/10]$. With the passage of time, a steady cellular structure developed, quite similar to that shown in Fig. 1. It would be of interest to do some numerical experiments with the two-dimensional equation (37) and to see whether it generates hexagonal structures of the solidification front.

Acknowledgments

The author wishes to thank Professor J.S. Langer for a stimulating discussion. This research was jointly supported by the Israel Commission for Basic Research and by the Director, Office of Energy Research, Office of Basic Energy Sciences, Engineering, Mathematical, and Geosciences Division of the U.S. Department of Energy under contract DE-AC03-76SF00098.

References

1. Kuramoto, Y. and Tsuzuki, T., 1976, Prog. Theor. Phys. **55**, 356.
2. Lin, J. and Kahn, P.B., 1980, Lecture Notes in Physics, **132**, 345.
3. Sivashinsky, G.I., 1977, Acta Astronaut. **5**, 1177.
4. Sivashinsky, G.I. and Michelson, D.M., 1980, Prog. Theor. Phys. **63**, 2112.
5. Chapman, C.J. and Proctor, M.R.E., 1980, J. Fluid Mech. **101**, 759.
6. Sivashinsky, G.I., 1981, Physica D: Nonlinear Phenomena (to appear).
7. Newell, A.C. and Whitehead, J.A., 1969, J. Fluid Mech. **38**, 279.
8. Langer, J.S., 1980, Rev. Mod. Phys. **52**, 1.
9. Mullins, W.W. and Sekerka, R.F., 1964, J. Appl. Phys. **35**, 444.
10. Wollkind, D.J. and Segel, L.A., 1970, Phil. Trans. Roy. Soc. (London) **268A**, 351.
11. Gertsberg, V.L. and Sivashinsky, G.I., 1981, Prog. Theor. Phys. **66**, 1219.

Figure Captions

- Fig. 1. Diagram illustrating directional-solidification experiment.
- Fig. 2. Neutral stability curves for different K values. $(\partial W(k, K) / \partial K < 0)$.
- Fig. 3. Rate of stability parameter ω vs. disturbance wavenumber k .
($W < W_c$).
- Fig. 4. Stationary cellular structures generated by Eq. (39).

Fig. 1

Fig. 2

Fig. 3

Fig. 4

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720