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Solidification fronts with unusual long-time behavior

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Precisely at a critical undercooling Δ_c, one-dimensional solidification fronts can travel with a velocity v, which scales in time as $t^{-1/3}$. This result, recently found in computer simulations and explained on dimensional grounds, is derived here from the starting equations.

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One-dimensional solidification fronts are well known to have two qualitatively different types of long-time behavior [1]. For small undercoolings, front growth is dominated by the need to allow heat to diffuse away, and the front advances in time as $t^{1/2}$. This result was derived by Zener [2], together with explicit expressions for the temperature profile. For undercoolings greater than a critical value Δ_c, the heat released as the front advances is not great enough to bring liquid adjacent to the front above the melting temperature, and the front travels at a constant velocity [1,3], limited only by the rate at which liquid can transform into solid.

Quite recently, this scenario has been examined in detail and found incomplete. The difficulties occur for undercoolings precisely equal to Δ_c, right on the border between steady-state and diffusive behavior. The states found by Zener, advancing as $t^{1/2}$, are not viable at Δ_c. Sometimes steady states exist, but when certain conditions on the relative diffusion rates of heat and solid are met, they can be proved not to exist [4–6]. What will be the long-time behavior of the fronts in this case? Numerical simulations of Löwen, Bechhoefer, and Tuckerman [7] find fronts growing with $v \sim t^{-\alpha}$, where α adopts a range of values near to $\frac{1}{3}$. A simple dimensional argument due to Oswald [8] leads one to expect fronts growing as $v \sim t^{-1/3}$. The purpose of this paper is to derive the appropriate long-time states analytically. Theory predicts that fronts do eventually grow with $v \sim t^{-1/3}$, but that very long transients prevent rapid appearance of the asymptotic state, explaining the apparent variability of exponents measured in the numerical simulations.

Figure 1 illustrates the setting of the problem. A solid, whose order parameter is indicated by a solid line, advances into a liquid from left to right at velocity $v(t)$. The transformation from liquid to solid is accompanied by a release of heat, and the resulting temperature profile is indicated by the dashed line. The transformation proceeds because far to the right the liquid is undercooled to a temperature $u(\infty)$ below the freezing point. In dimensionless form, equations to describe this process are [9]

$$u_t = \frac{1}{2p} u_{zz} + m_t , \tag{1}$$

$$m_t = \frac{1}{2} m_{zz} - \frac{\partial f_0}{\partial m} - \frac{\delta u}{2} . \tag{2}$$

The temperature field is described by u, and the order parameter, which would represent entropy density for a liquid-solid transition, is described by m. The constant p gives the ratio of the diffusion rate of m to the diffusion rate of u, while δ indicates the strength of the coupling between m and u. The function $f_0(m)$ is any reasonable potential with two minima of equal height—one at $m=0$ and the other at $m=1$. When a definite form is needed,

$$f_0 = \tfrac{1}{2} \min[m^2, (1-m)^2] \tag{3}$$

will be used, but the particular form will not be important [10].

There is a correspondence between the model described in Eqs. (1) and (2), and a model with a sharp interface [11], which in the present case becomes exact at late times. The sharp-interface model may be obtained from two observations. First, as the fields evolve, right in the vicinity of the interface they do not change shape appreciably, but simply translate at some velocity $v(t)$. Very close to the interface, one can replace $\partial/\partial t$ by $-v\partial/\partial z$.

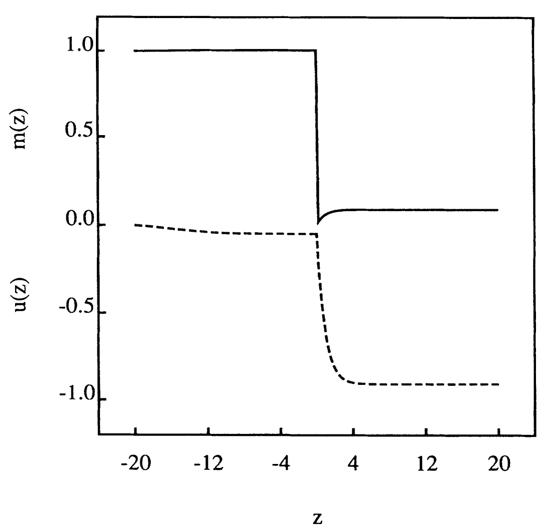

FIG. 1. A solid advances into an undercooled liquid. The solid occurs where the solid line is near 1, while the liquid is defined by the region where the solid line is near 0. The temperature field is given by the dashed line. The diagram illustrates the analytical solution found in the text for $\delta=0.2$, $p=1$, $\sigma=1$, and $\lambda=80$.

Second, when viewing the interface as infinitely sharp, the order parameter m changes discontinuously from some value near 0 to some value near 1 within the interface, but the temperature field is continuous (although the first derivative of temperature is not). Letting superscripts $-$ and $+$ refer to values on the left- and right-hand sides of the interface, respectively, integrate Eq. (1) from the left side of the interface to the right. One has that

$$v(m^+ - m^-) = \frac{1}{2p}(u_z^+ - u_z^-) . \tag{4}$$

Multiplying Eq. (2) by m_z and integrating across the interface likewise gives

$$-v\sigma = \tfrac{1}{2}[(m_z^+) - (m_z^-)] - [f_0(m^+) - f_0(m^-)] - \frac{\delta u^0}{2}(m^+ - m^-) . \tag{5}$$

Here

$$\sigma = \int_-^+ dz\,(m_z)^2$$

is the surface tension [12] and u^0 is the temperature at the interface. With these two boundary conditions in hand, it is possible to ignore nonlinearities of f_0 within the interface, and treat a linear boundary-value problem.

It is useful to introduce the scaled position

$$\hat{z} = (z - l)/\lambda ,$$

and consider u and m to be functions of $\hat{z}$ and $\lambda(t)$. The location of the interface is given by $l(t)$ (that is, $\hat{z} = 0$), so $\dot{l} = v$, while $\lambda(t)$ is defined as the decay length of the temperature field to the right of the interface:

$$\lambda \equiv -\frac{u_z^+}{u_{zz}^+} \Longrightarrow \frac{u_{\hat{z}}^+}{u_{\hat{z}\hat{z}}^+} = 1 . \tag{6}$$

The basic assumption is that in these new variables, Eqs. (1) and (2) take the scaling form

$$(m_{\hat{z}} - u_{\hat{z}})(v\lambda + \dot{\lambda}\lambda\hat{z}) = \frac{1}{2p}u_{\hat{z}\hat{z}} , \tag{7}$$

$$m_{\hat{z}}(v\lambda + \dot{\lambda}\lambda\hat{z}) + \frac{1}{2}m_{\hat{z}\hat{z}} = \left[\frac{\partial f_0}{\partial m} + \frac{\delta u}{2}\right]\lambda^2 . \tag{8}$$

Terms such as $m_\lambda\dot{\lambda}$ have been dropped, since they turn out to be negligible at late times. Attention is now directed to the possibility of scaling states with $\lambda \sim t^a$, where $a > 0$. The assumption that the equations should largely be time independent in the new coordinates appears to be jeopardized by the right-hand side of Eq. (8), which grows as λ^2. The difficulty is avoided by assuming that

$$n(\hat{z}) \equiv \left[\frac{\partial f_0}{\partial m} + \frac{\delta u}{2}\right]\lambda^2$$

is time independent at long times. Physically, this assumption means that the order parameter is very close to its equilibrium value everywhere outside of the interface. Using Eq. (3) to fix the form of f_0, one has

$$m = n/\lambda^2 + \Theta(-\hat{z}) - \delta u/2 .$$

The late-time state will soon be seen to be determined by terms up to order λ^{-1}, so one can take

$$m = \Theta(-\hat{z}) - \delta u/2 . \tag{9}$$

Using Eq. (9) and defining $\Delta_c = (1 + \delta/2)^{-1}$, one can rewrite Eqs. (4), (5), and (7) as

$$2pv\lambda = u_{\hat{z}}^- - u_{\hat{z}}^+ , \tag{10}$$

$$u^0 = -2v\sigma/\delta , \tag{11}$$

$$u_{\hat{z}}(v\lambda + \dot{\lambda}\lambda\hat{z}) = -(\Delta_c/2p)u_{\hat{z}\hat{z}} . \tag{12}$$

From Eqs. (6) and (12) one finds the useful relation

$$\lambda v = \Delta_c/2p . \tag{13}$$

The solution of Eq. (12), with boundary conditions Eqs. (10) and (11), is straightforward. To the left of the interface,

$$u(\hat{z}) = \frac{-2v\sigma}{\delta}\left[\frac{\dot{\lambda}}{2\pi v}\right]^{1/2} e^{-v/2\dot{\lambda}} \int_{-\infty}^{\hat{z}} d\hat{z}' e^{-\hat{z}' - \dot{\lambda}(\hat{z}')^2/2v} . \tag{14}$$

Note that although $\dot{\lambda}$ is very small at late times, the solution would not be physically sensible if $\dot{\lambda}$ were set to zero. From Eqs. (10) and (12), one finds, up to exponentially small corrections, that on the right-hand side of the interface

$$u(\hat{z}) = \Delta_c \int_{\hat{z}}^{\infty} d\hat{z}' e^{-\hat{z}' - \dot{\lambda}(\hat{z}')^2/2v} + u(\infty) . \tag{15}$$

Expanding $e^{-\dot{\lambda}(\hat{z}')^2/2v}$ as a power series in $\dot{\lambda}$ to first order [13] implies, with use of Eq. (11), that

$$u^0 = \frac{-2v\sigma}{\delta} = \Delta_c\left[1 - \frac{\dot{\lambda}}{v}\right] + u(\infty) + O(\dot{\lambda}^2) . \tag{16}$$

The Zener [2] solutions are obtained if one assumes that $\dot{\lambda}/v$ scales as a constant. However, there is a second possibility, which is that $\dot{\lambda}/v$ scales in the same way as v. Since from Eq. (13) λv is constant, one finds that $\lambda \sim t^{1/3}$. By requiring the terms multiplying separate powers of t in Eq. (16) to vanish separately, one obtains

$$u(\infty) = -\Delta_c ,$$
$$\lambda = \left[\frac{3\sigma\Delta_c}{2\delta p^2}t\right]^{1/3} , \quad v = \left[\frac{\delta\Delta_c^2}{12p\sigma t}\right]^{1/3} . \tag{17}$$

The fields shown in Fig. 1 illustrate the shape of this solution. The prefactors in Eq. (17) agree within 1% with the values obtained at the longest times from numerical simulation [7,13].

The analysis itself predicts that these scaling states can exist only at the critical undercooling $u(\infty) = -\Delta_c$. However, even then, these states are not always selected dynamically. It has been found [4–7] that for $p \gtrsim 2/(3\delta)$, steady-state solutions are allowed at Δ_c. Because steady-state solutions grow faster than those with $v \sim t^{-1/3}$, dynamics should select them. Only when steady states are forbidden should the states with $v \sim t^{-1/3}$ appear.

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[9] The model is known as the phase-field model, or model C of critical dynamics, defined by P. C. Hohenberg and B. I. Halperin, Rev. Mod. Phys. **49**, 435 (1977), who also give the connection between the dimensionless parameters used here and physically measurable constants.

[10] The symmetry between the two minima could be eliminated; the algebra would be slightly more complicated.

[11] The reduction from phase-field to sharp-interface models, carried out cavalierly here, has been looked at in detail, and with attention to possible problems, by G. Caginalp, Rocky M. J. Math. **21**, 603 (1991); Phys. Rev. A **39**, 5887 (1989). For the purposes of the present calculations, it would have been perfectly satisfactory to begin with a sharp-interface model and a kinetic term, but as all of the recent literature is in terms of the phase-field model, it seemed desirable to emphasize the connection.

[12] The velocity dependence of the surface tension becomes negligible at late times.

[13] The steady state has been reached only when subsequent terms in this expansion are negligible. From Eqs. (16) and (17) one gets the estimate that to achieve fractional accuracy A, $t \gg A^{-3}\sigma^2/(\Delta_c \delta^2 p)$. For $A \sim 0.01$, $\delta \sim 0.1$, $p=\sigma=1$, one needs $t \sim 10^8$. This observation explains the long transients in the numerical simulations of Ref. [7].