Diffusion disallowed crystal growth. II. A parabolic model

Hartmut Löwen,[a] Sarah A. Schofield, and David W. Oxtoby
James Franck Institute, University of Chicago, 5640 South Ellis Avenue, Chicago, Illinois 60637

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The growth of a crystal into an undercooled liquid is studied within a phase field model. In contrast to the usual Landau–Ginzburg approach, the free energy as a function of the order parameter is taken to be a pair of intersecting parabolas. This model is completely solvable and shows a transition from heat-diffusion allowed to disallowed steady-state crystal growth. Analytical expressions for the interface velocity and for the order parameter and temperature profiles are obtained and extensively discussed. In comparison with the Landau–Ginzburg model, most qualitative and quantitative features are the same. However, the solution of the present model is more general, avoiding perturbation theory, and gives a clearcut picture of the underlying transition.

I. INTRODUCTION

The kinetics of a first-order transition is governed by two dynamical processes: nucleation and growth. The rates and mechanisms of nucleation and growth are important in a number of applications. The crystallization of metals and metal alloys significantly affects their microstructures and thus many of their mechanical properties.[1] The phase separation and crystallization of compounds from molten magmas has a profound effect on the distribution and morphology of minerals in natural ores. First-order solid–solid phase transitions (such as order–disorder[2] or martensitic[3] transitions) also play an important role in materials science.

Nucleation corresponds to the first appearance of the new phase as a fluctuation in the original phase; if the cost in free energy to create the critical nucleus of the new phase is large enough, the rate can be quite small and the original phase can persist in a metastable state for a considerable period of time.[4] The growth process involves the propagation of a stable phase into the unstable phase and can be controlled by several factors. One of these is the rate of attachment of individual atoms or molecules to the new phase across the interface, and another is the rate of disposal of the heat evolved in the phase transition. As latent heat is produced in an undercooled system, the temperature rises and the driving force for growth is reduced.

It thus appears evident that a full theory of the kinetics of growth in a first-order transition would involve the variation in space and time of at least two quantities: an order parameter that distinguishes the two phases, and the temperature, which affects the local driving force for the formation of the new phase. Most theories, however, include one or the other of these quantities but not both. The "standard model" for growth[5] assumes that the phase boundary is infinitely narrow, so that the order parameter changes discontinuously across it. It is treated as a delta-function source of heat, and the equation to be solved is the heat flow equation with a moving boundary condition. On the other hand, "kinetic" models for growth[6] assume a uniform temperature through the interface and calculate the velocity of the propagating interface as a function of the driving force for the transition.

In a recent paper two of us examined the steady-state solutions of the coupled equations for temperature and a nonconserved order parameter in one dimension.[7] In agreement with earlier work,[8] we found that incorporation of the order parameter equation gave "velocity selection." Whereas in the standard model all velocities are possible, the introduction of a finite order parameter length and time scale allows at most one particular steady-state velocity to occur for a propagating interface. The surprising result from Ref. 7 was that such steady-state solutions do not exist for all choices of system parameters. If the thermal diffusivity becomes large enough (or, equivalently, if the latent heat becomes small enough), the solutions abruptly disappear at a critical value.

Reference 7 employed a quartic Landau–Ginzburg free energy as a function of order parameter (a ϕ^4 field theory). Although this is the simplest smooth form of the free energy that allows a first-order transition, it has some disadvantages. First, because of the nonlinear nature of the order parameter derivative of the free energy, analytic solutions for the critical point at which steady-state solutions exist are possible only in the limit of weak coupling of temperature and order parameter dynamics. For larger couplings, numerical techniques were needed to explore the dynamics, and the equations became increasingly stiff as the critical point was approached because of the growing disparity in length scales between temperature and order parameter. Second, examination of the time-dependent behavior in the region where steady-state solutions no longer exist was numerically too time consuming to attempt.

In this paper, we examine the solution of the coupled equations for temperature and order parameter dynamics for a different free energy, one which consists of a pair of intersecting parabolas. This gives differential equations that are piecewise linear, so that analytical solution is possible for arbitrary coupling between order parameter and temperature. Such a model was used earlier by two of us to study the "kinetic model" for growth of a nonconserved order param-

[a] Present address: Laboratoire de Physique, Ecole Normale Supérieure de Lyon, 46 Allée d'Italie, F-69364 Lyon Cedex 07, France. Permanent address: Sektion Physik der Universität München, Theresienstrasse 37, D-8000 München 2, West Germany.

eter at a fixed temperature.[9] Here we find that the qualitative features found for the quartic Landau–Ginzburg model in the earlier work are robust; the same conclusion results that for large enough thermal diffusivity the one-dimensional steady-state solutions cease to exist. We can now go much farther with the equations, however, and draw conclusions that were explored only numerically or not at all in the earlier work.

In Sec. II, we outline the general theory for coupled temperature and order parameter dynamics and introduce the new free energy functional. The calculation and results of Sec. III describe the steady-state solutions, which we show vanish above a critical value of the thermal diffusivity. Section IV describes the method for calculation of relaxation to the steady state, and of growth kinetics where the steady state no longer exists. Section V points to some general conclusions.

II. GENERAL THEORY

The general formulation of the theory begins with a consideration of one hydrodynamic variable, here the temperature, coupled to one nonconserved order parameter. This produces a phase field model, embodied in the following equations:[8–10]

$$\frac{\partial u}{\partial t} = \alpha \nabla^2 u + \frac{\partial m}{\partial t}, \tag{2.1}$$

$$\frac{\partial m}{\partial t} = -\frac{\Gamma}{\rho_0} \frac{\delta F}{\delta m}\bigg|_{T_0} - \gamma u. \tag{2.2}$$

The two variables are m, a nonconserved order parameter, normalized to be 0 in the liquid and 1 in the solid, and $u = c(T - T_0)/L$, a reduced temperature, where L is the latent heat of fusion, c the heat capacity, and T_0 the equilibrium coexistence temperature. The other parameters are the thermal diffusivity α, the kinetic relaxation rate Γ, the bulk number density ρ_0, and a coupling parameter γ, equal to $\Gamma L^2/k_B c T_0^2$. These equations will be applied to a one-dimensional system. We take as the free energy per unit area A of interface (measured in units of $k_B T_0$)

$$\frac{F}{A} = \int_{-\infty}^{\infty} dz\, \rho_0 \left[\frac{1}{2} K^2 \left(\frac{\partial m(z,t)}{\partial z}\right)^2 + f(m(z,t))\right] - \frac{1}{4}\int_{-\infty}^{\infty} dz \int_{-\infty}^{\infty} dz'\, w(|z-z'|)(m(z,t) - m(z',t))^2. \tag{2.3}$$

The first, square-gradient, term accounts for correlations in the system with K the correlation length. The second term consists of the local free energy $f(m)$, that is the free energy which a spatially uniform system with order parameter m and temperature $u = 0$ would have. The last term is a nonlocal term which can account for long range interactions. The importance of such interactions in an application to surface melting was pointed out in Ref. 11.

The particular version of the model depends on the form that is assumed for the local free energy $f(m)$. Using the common Landau–Ginzburg (ϕ^4) form,

$$f(m) = Em^2(m-1)^2 \tag{2.4}$$

gives a continuous though nonlinear kinetic equation. $E/16$ is the height of the barrier between the two wells in the free energy $f(m)$. The combined model of Eqs. (2.1)–(2.4), with $w = 0$, has been studied by two of us[7] for steady-state one dimensional growth, with analytic solutions obtained by treating γ as a small parameter. Another set of equations results from using a double parabola model,

$$f(m) = \max\left[\frac{\lambda}{2} m^2, \frac{\lambda}{2}(m-1)^2\right], \tag{2.5}$$

which gives a piecewise linear kinetic equation. Here λ is a parameter that can be used to adjust the height of the intersection of the two parabolas relative to the barrier height E of Eq. (2.4). Letting $\lambda = E/2$ allows the barrier heights to match, whereas when $\lambda = 2E$ the curvatures of the minima at $m = 0$ and $m = 1$ match (Fig. 1). These two bounding values of λ will be used in later sections to compare the results of using the two equations (2.4) and (2.5). Using the parabola model, the kinetic equation includes a step function at the intersection z_0 of the parabolas. Equations (2.2)–(2.3), and (2.5) are then supplemented by a boundary condition locating this intersection at the interface, that is

$$m(z_0) = \tfrac{1}{2}. \tag{2.6}$$

The combined model of Eqs. (2.2), (2.5) and (2.6) for constant u has been studied by two of us[9] for, among other situations, steady-state one-dimensional motion, exactly in γ. (The product γu here replaces ε of Ref. 9.) This exactness in γ is a significant advantage of using Eqs. (2.5) and (2.6) rather than (2.4) to obtain steady-state solutions, because it applies also when Eq. (2.1) is included; this is not the case for the Landau–Ginzburg kinetic model. It will be shown in the following section that the result of the critical dependence of the steady-state velocity on α, obtained treating γ as a perturbation in the Landau–Ginzburg model of Eqs.

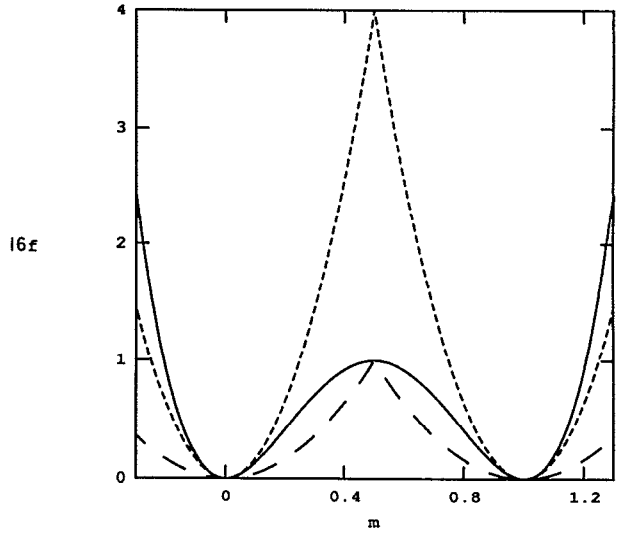

FIG. 1. The local free energy as a function of order parameter, for the parabola model, with $\lambda = 1/2$ (long dashed line) and $\lambda = 2$ (short dashed line); and for the Landau–Ginzburg model with $E = 1$ (solid line).

(2.1)–(2.4), can be obtained also using the parabola model of Eqs. (2.1)–(2.3), (2.5) and (2.6), however, exactly in γ.

III. STEADY-STATE SOLUTIONS

We now look for steady-state solutions for the general equations of motion (2.1) and (2.2) in one dimension. These will depend only on the variable $z - vt$, v being the velocity, and not separately on z and t. Introducing $l_m = K\sqrt{2/\lambda}$ and $\tau_m = 1/\lambda\Gamma$ as natural length and time scales, respectively, we get the following steady-state equations, where for simplicity $(z - vt)/l_m$ has been replaced by z and v is now the dimensionless velocity in units of l_m/τ_m:

$$-vu_z = \frac{1}{2p}u_{zz} - vm_z, \tag{3.1}$$

$$-vm_z = -m + \theta(-z) + \tfrac{1}{2}m_{zz} - \int dz\, w(z-z')[m(z') - m(z)] - \frac{\delta u}{2}. \tag{3.2}$$

Derivatives are indicated by subscripted letters, and $\theta(z)$ is a step function. The key dimensionless parameters $p = K^2\Gamma/\alpha$ and $\delta = 2L^2/(\lambda k_B c T_0^2)$ have been introduced, and the function $w(z)$ has been made dimensionless.

We intend to perform an analytical solution of the coupled integro-differential equations (3.1) and (3.2) as far as possible. The basic idea is to apply Fourier transformation defined as follows for a z-dependent function $b(z)$:

$$\hat{b}(k) = \int_{-\infty}^{\infty} dz\, e^{ikz} b(z). \tag{3.3}$$

The back transform is

$$b(z) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dk\, e^{-ikz}\hat{b}(k). \tag{3.4}$$

We can summarize (3.1) and (3.2) in the following matrix equations:

$$\begin{pmatrix} ikv + \dfrac{k^2}{2p} & -ikv \\ \dfrac{\delta}{2} & ikv + \dfrac{k^2}{2} + 1 + W(k) \end{pmatrix} \begin{pmatrix} \hat{u}(k) \\ \hat{m}(k) \end{pmatrix} = \begin{pmatrix} iCk\delta(k) \\ \displaystyle\int_{-\infty}^{0} dz'\, e^{ikz'} \end{pmatrix} \tag{3.5}$$

with

$$W(k) = w(k) - w(0). \tag{3.6}$$

Here, C is a purely real constant which is determined by fixing the boundary conditions of the problem. The final result for $u(z)$ and $m(z)$ can be obtained by matrix inversion and back transformation, yielding

$$u(z) = u_0 + \frac{1}{2\pi}\int_{-\infty}^{0} dz' \int_{-\infty}^{\infty} dk\, e^{ik(z'-z)} \frac{ikv}{D(k)} \tag{3.7}$$

and

$$m(z) = m_0 + \frac{1}{2\pi}\int_{-\infty}^{0} dz' \int_{-\infty}^{\infty} dk\, e^{ik(z'-z)} \frac{ikv + k^2/2p}{D(k)} \tag{3.8}$$

with the abbreviation

$$D(k) = \left(ikv + \frac{k^2}{2p}\right)\left[ikv + \tfrac{1}{2}k^2 + 1 + W(k)\right] + \frac{ik\delta v}{2}. \tag{3.9}$$

Here,

$$u_0 = \frac{C}{2\pi v[1 + (\delta/2)]}, \quad m_0 = \frac{-\delta C}{4\pi v}\left(1 + \frac{\delta}{2}\right)^{-1}.$$

We study situations where $u(-\infty) = 0$. Hence $C = -2\pi v$ and

$$u_0 = -\frac{1}{[1 + (\delta/2)]}, \tag{3.10}$$

$$m_0 = \frac{\delta}{2}\frac{1}{[1 + (\delta/2)]}. \tag{3.11}$$

The other boundary conditions are then

$$u(\infty) = \frac{-1}{[1 + (\delta/2)]} m(-\infty) = 1,$$

$$m(\infty) = \frac{\delta/2}{[1 + (\delta/2)]}. \tag{3.12}$$

Notice that up to now v is not determined. An equation for v is obtained by the requirement [see Eq. (2.6)] $m(0) = 1/2$ which leads to the basic equation

$$\tfrac{1}{2} - m_0 = \frac{1}{\pi}\int_0^{\infty} dz \int_{-\infty}^{\infty} dk\, e^{-ikz} \times \frac{k + 2ipv}{(k + 2ipv)(2ikv + k^2 + 2 + 2W(k)) + 2i\delta vp}. \tag{3.13}$$

We emphasize that we have obtained *analytical* expressions for the steady-state profiles, see Eqs. (3.7) and (3.8), as well as for the interface velocity v, given as a root of Eq. (3.13). From now on we simplify our model further by assuming $W(k)$ to be zero; that is, we neglect nonlocal long range interactions for the order parameter. Then a complete analytical treatment is possible.

First of all, one has to find the zeros of the cubic expression in k in the denominators of Eq. (3.13) and of $D(k)$ in Eqs. (3.7) and (3.8). After integrating over k in the complex plane, the remaining space integration can also be evaluated analytically. Let us first describe the result for Eq. (3.13). Define

$$r = v(2p + 2), \quad s = -(2 - 4p^2), \quad t = -2pv(2 + \delta) \tag{3.14}$$

and

$$p' = \frac{3s - r^2}{3}, \quad q = \frac{2r^3}{27} - \frac{rs}{3} + t, \quad d = \frac{p'^3}{27} + \frac{q^2}{4}. \tag{3.15}$$

The nature of the solutions depends on the sign of d. If $d \leqslant 0$ (which is the normal case in our problem), define

$$\rho = \sqrt{-p'^3/27}, \quad \phi = \arccos\left(\frac{-q}{2\rho}\right), \tag{3.16}$$

and obtain three roots x_j as

$$\begin{aligned} x_1 &= 2\sqrt[3]{\rho}\cos\left(\frac{\phi}{3}\right) - \frac{r}{3}, \\ x_2 &= 2\sqrt[3]{\rho}\cos\left(\frac{\phi}{3} + \frac{2\pi}{3}\right) - \frac{r}{3}, \\ x_3 &= 2\sqrt[3]{\rho}\cos\left(\frac{\phi}{3} + \frac{4\pi}{3}\right) - \frac{r}{3}. \end{aligned} \tag{3.17}$$

In the opposite case, $d > 0$, define

$$y_1 = \sqrt[3]{-(q/2) + \sqrt{d}}, \quad y_2 = \sqrt[3]{-(q/2) - \sqrt{d}}, \tag{3.18}$$

and obtain three complex roots $x_j = ik_j$ given by

$$\begin{aligned} x_1 &= y_1 + y_2 - \frac{r}{3}, \\ x_2 &= -\tfrac{1}{2}(y_1 + y_2) + i\frac{y_1 - y_2}{2}\sqrt{3} - \frac{r}{3}, \\ x_3 &= -\tfrac{1}{2}(y_1 + y_2) - i\frac{y_1 - y_2}{2}\sqrt{3} - \frac{r}{3}. \end{aligned} \tag{3.19}$$

With these definitions the basic equation can be simplified as follows:

$$\tfrac{1}{2} - m_0 = 2\sum_{\mathrm{Re}\, x_j < 0} \frac{x_j + 2pv}{x_j \prod_{i \neq j}(x_j - x_i)} \tag{3.20}$$

which is an equation for the velocity. Thus a unique velocity is selected, as in the Landau–Ginzburg phase field model.[7] It is however more easily obtained and understood in the present parabolic model, from the variation of roots of a cubic equation.

For analytical results, let us first study the limiting case $p \to \infty$. Then simple algebra leads to the velocity

$$v_{\max} = \frac{\delta}{\sqrt{2 - \delta}}. \tag{3.21}$$

For comparison, the Landau–Ginzburg model of Ref. 7 gave the perturbation result $v_{\max} = 3\delta/4$. For smaller p, Eq. (3.20) can be solved numerically to obtain v. There is a nontrivial solution $v(p) > 0$ only for $p > p_c$, whereas for $p \leqslant p_c$ only the trivial equilibrium solution $v = 0$ is realized.[13] This is the same qualitative result as obtained with the Landau–Ginzburg form for $f(m)$: a large enough thermal diffusivity α prevents the existence of steady-state solutions.

An analytical expression can be obtained for p_c. Differentiating the right-hand side with respect to v and setting $v = 0$ gives p_c as a function of δ. One obtains the rather simple result

$$p_c = \frac{2}{3\delta} \tag{3.22}$$

The same result, $p_c\delta = 2/3$, was obtained in Ref. 7 from the Landau–Ginzburg free energy, but only as a perturbation result for very small δ. Recall, however, that δ is defined in terms of E in the earlier work and in terms of λ in this paper; therefore we have to choose $\lambda = E$ to fit this result. This is a situation intermediate between the two extreme cases of curvature fitting ($\lambda = 2E$) and barrier height fitting ($\lambda = E/2$). Further, comparing the results of the models, Eqs. (3.21) and (3.22) apply over the entire range of δ, giving a different quantitative dependence on δ.

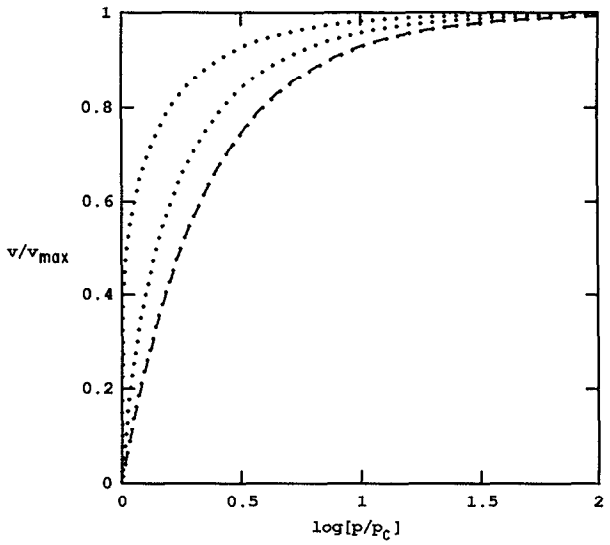

FIG. 2. Velocity as a function of p. The results of the parabola model (three dotted lines with δ_p equal to 0.2, 0.98, and 1.6 from bottom to top), showing a nonuniversality in δ in the parabola model. They are compared with the result of the perturbation calculation of the Landau–Ginzburg model (dashed line), for $\delta_{LG} = 0.1$.

In Figs. 2 and 3, the results of finding v numerically by solving Eq. (3.20) are shown and are compared to those from the Landau–Ginzburg free energy. The latter consists of a perturbation result valid only for small δ, and numerical data for higher δ. From Fig. 2, the Landau–Ginzburg results for $\delta = 0.1$ are nearly identical to those of the present calculation for $\delta = 0.2$. This means that the correspondence $\lambda = E/2$ (barrier height fitting) gives results in close agreement between the two calculations, and suggests that the barrier rather than the curvature is crucial for comparing the different models. The scaling assumption of Ref. 7 states that in a plot of $v/v_{\max}$ against $\log(p/p_c)$ all points fall on one curve. Within our model we examined this (Fig. 2) and find an explicit dependence on δ. In particular, $v/v_{\max}$ increases for fixed p but increasing δ. This shows that the scaling assumption is not generally valid. Concerning the numerical data for v (see Fig. 3) we mention that they lie within their error bars between the two extreme cases $\lambda = 2E$ and $\lambda = E/2$. This shows consistency between the two models used.

Let us now discuss the steady-state profiles. Calculating the integrals in Eqs. (3.7) and (3.8) gives the following results:

$$\begin{aligned} \begin{pmatrix} u(z) \\ m(z) \end{pmatrix} &= \begin{pmatrix} u_0 \\ m_0 \end{pmatrix} + 2\sum_{\mathrm{Re}\, x_j < 0} \frac{1}{x_j \prod_{i \neq j}(x_j - x_i)} \begin{pmatrix} 2pv \\ 2pv + x_j \end{pmatrix} \\ &\quad + 2\sum_{\mathrm{Re}\, x_j > 0} \frac{1}{x_j \prod_{i \neq j}(x_j - x_i)} \\ &\quad \times \begin{pmatrix} 2pv \\ 2pv + x_j \end{pmatrix} (1 - e^{x_j z}) \end{aligned} \tag{3.23}$$

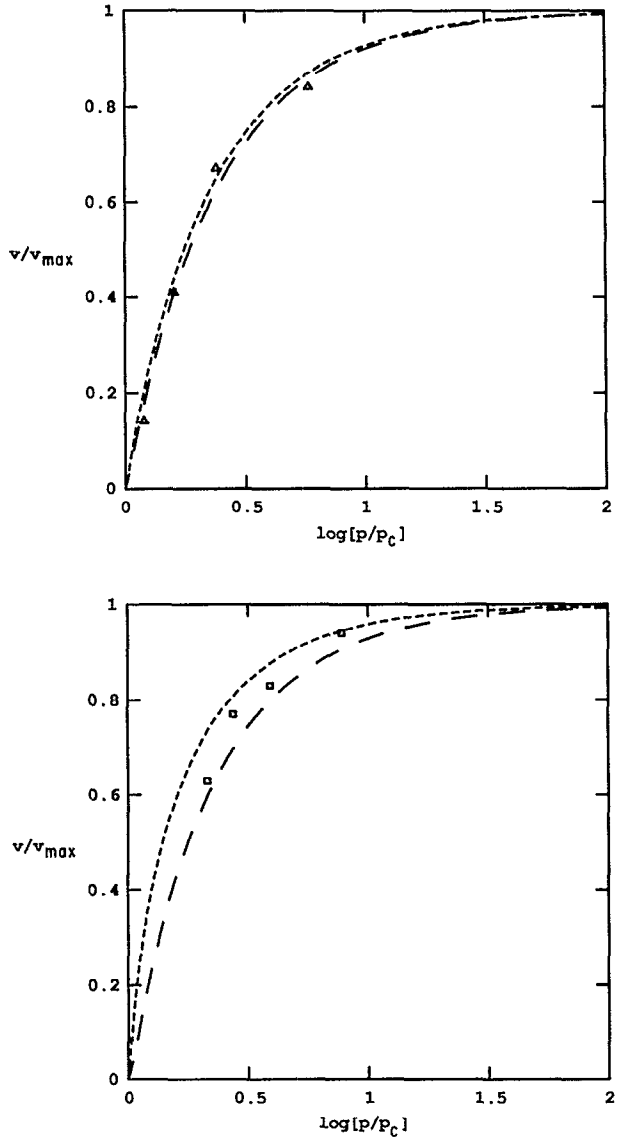

FIG. 3. Velocity as a function of p. The results of the parabola model ($p_c = 2/3\delta$) are compared with the scaled results ($p_c = 1/2v_{max}$) of the numerical calculation of the Landau–Ginzburg model. (a) $\delta_{LG} = 0.1$ (triangles), compared with $\delta_P = 0.05$ (short dashed lines) and $\delta_P = 0.2$ (long dashed lines). (b) $\delta_{LG} = 0.49$ (squares), compared with $\delta_P = 0.245$ (short dashed lines) and $\delta_P = 0.98$ (long dashed lines).

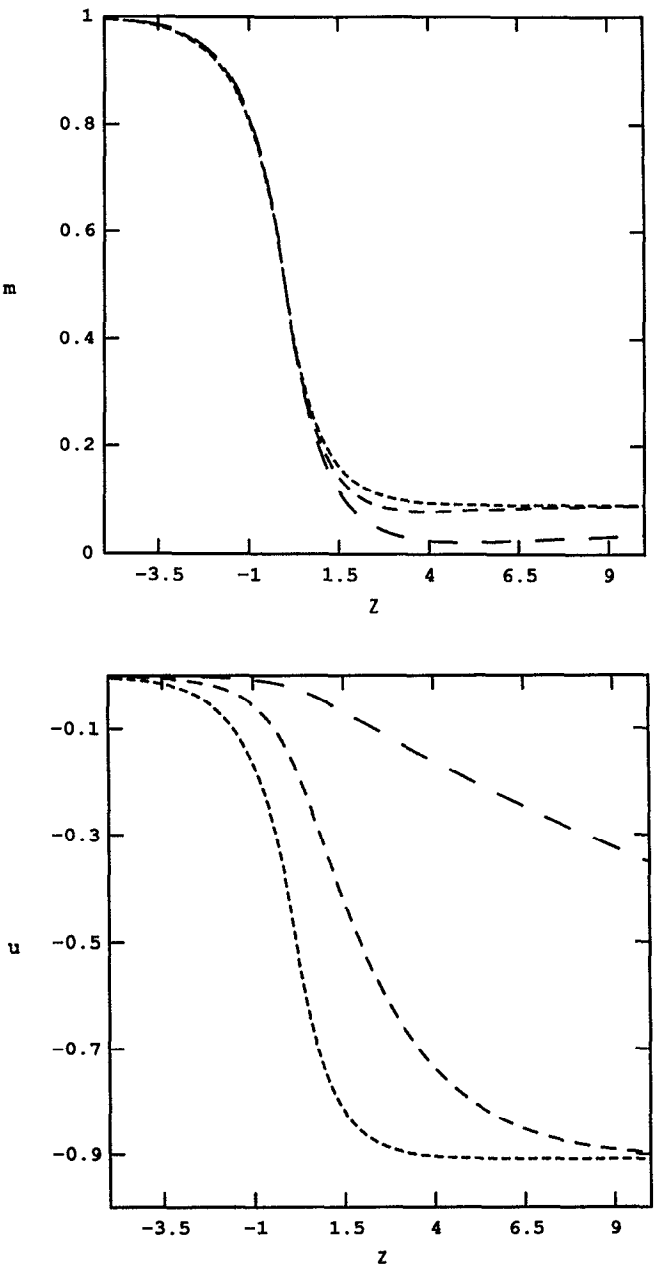

FIG. 4. Spatial profiles, calculated with the parabola model for $\delta = 0.2$. The z axis is in units of $l_m/\sqrt{2}$ and the interfacial point $m = 1/2$ is at $z = 0$. The values of p/p_c are 9 (short dashed lines); 1.5 (dashed lines) and 1.05 (long dashed lines) for (a) the order parameter and (b) the temperature.

for $z \leqslant 0$ and

$$\begin{pmatrix} u(z) \\ m(z) \end{pmatrix} = \begin{pmatrix} u_0 \\ m_0 \end{pmatrix} + 2 \sum_{\mathrm{Re}\, x_j < 0} \frac{e^{x_j z}}{x_j \prod_{i \neq j} (x_j - x_i)} \times \begin{pmatrix} 2pv \\ 2pv + x_j \end{pmatrix} \tag{3.24}$$

for $z > 0$. Here the x_j are given by the definitions (3.14)–(3.19). These analytical expressions are displayed graphically in Fig. 4. Here we keep δ fixed and choose three different values for p, one of them being very near to p_c. As p_c is approached $u(z)$ becomes longer and longer ranged up to the point $p = p_c$. At this point, heat diffusion is large enough to prevent the crystal from growing in a steady-state manner.

On the other hand, the corresponding order parameter profiles, $m(z)$, show no drastic variation in their interfacial widths as p decreases. However, since m follows the temperature which is not at its boundary value, it overshoots the boundary value considerably on the liquid side, resulting in a nonmonotonic behavior.

Another interesting remark concerns the existence of x_i's with nonvanishing imaginary parts [the case $d > 0$ in

Eqs. (3.18) and (3.19)]. As one sees easily from the explicit expressions (3.23) and (3.24) for the u and m profiles, this corresponds to an oscillatory behavior in the wings of the profiles. From our numerical analysis, we generally can exclude such a phenomenon for $p \simeq p_c$ and for very large p. However, for intermediate values (e.g, $\delta = 0.2, p = 10$), we find this oscillatory behavior on the liquid side of the system. We must mention, however, that this effect is scarcely visible because the imaginary parts of x_2 and x_3 are very small (0.127 for the parameters quoted above, which corresponds roughly to a length of one oscillation of 50 l_m). Therefore it is not at all visible in a plot as in Fig. 4. The physical origin is somewhat obscure. The system tends to develop heat waves into the undercooled liquid as the crystal grows in a steady-state manner. This is similar to the qualitative shape of the order parameter profile for the kinetic depinning transition studied by Meister and Müller-Krumbhaar.[12]

In conclusion, our model shows the same qualitative behavior as the previously studied model. However, a nearly complete analytical treatment is possible and perturbation theory in δ is not necessary. The underlying mathematical reason for the transition to heat diffusion disallowed growth becomes more transparent. As a function of δ and p, the solvability of a transcendental equation for v [see Eq. (3.10)] decides whether there is a steady-state solution or not.

IV. BEYOND THE STEADY STATE

In this section we focus on an analytical treatment of the *full* equations (2.1) and (2.2). The general method was developed in an earlier paper by two of us[9] for a one-variable system. The generalization to the present two-variable system (u,m) does not entail conceptual difficulties but the calculations are more tedious. Therefore we do not carry them out in great detail because they are similar in spirit to those of Ref. 9. In order to have a definite starting point, let us return to Eqs. (2.1) and (2.2) rewritten in the reduced time and space units defined at the beginning of Sec. III:

$$\frac{\partial u}{\partial t} = \frac{1}{2p}\frac{\partial^2 u}{\partial z^2} + \frac{\partial m}{\partial t}, \tag{4.1}$$

$$\frac{\partial m}{\partial t} = -m + \theta(z_0(t) - z) + \frac{1}{2}\frac{\partial^2 m}{\partial z^2} - \int dz'\, w(z-z')[m(z') - m(z)] - \frac{\delta u}{2}. \tag{4.2}$$

We can rewrite this as

$$L\begin{pmatrix} u \\ m \end{pmatrix} = \begin{pmatrix} 0 \\ \theta(z_0(t) - z) \end{pmatrix}, \tag{4.3}$$

where

$$L = \begin{pmatrix} \frac{\partial}{\partial t} - \frac{1}{2p}\frac{\partial^2}{\partial z^2} & -\frac{\partial}{\partial t} \\ \frac{\delta}{2} & \frac{\partial}{\partial t} - \frac{\partial^2}{\partial z^2} + 1 + \hat{W} \end{pmatrix} \tag{4.4}$$

is a linear nonsymmetric operator. In Eq. (4.4), $\hat{W}$ denotes the nonlocal linear integral operator defined by $\hat{W}m = \int dz'\, w(z-z')\,(m(z') - m(z))$.

The quantity $z_0(t)$ represents the position where the order parameter profile moves from one parabola to the other. In a first step, it is assumed to be known, but it has to be determined implicitly later. This was the main idea of the exactly soluble model in Ref. 9; the nonlinearity of the starting equations is hidden in $z_0(t)$. Equation (4.3) can then generally be solved by Green's function techniques. Let us define a 2×2 matrix, $G(z,t)$, as the solution of the matrix equation

$$LG(z,t) = I\delta(z)\delta(t) \tag{4.5}$$

where I is the 2×2 unit matrix. Then $G(z,t)$ can explicitly be calculated by Fourier transformation. In order to give the final result in a condensed form, we define two functions e and f by

$$e(k) = \frac{1}{2}\left[\left(\frac{1}{2} + \frac{1}{2p}\right)k^2 + 1 + W(k) + \delta\right], \tag{4.6}$$

$$f(k) = e^2 - \frac{1}{2p}k^2\left[\frac{1}{2}k^2 + 1 + W(k)\right], \tag{4.7}$$

where $W(k)$ is given by Eq. (3.6). Let us now introduce two frequencies

$$\omega_1(k) = e(k) - \sqrt{f(k)}, \quad \omega_2(k) = e(k) + \sqrt{f(k)}. \tag{4.8}$$

Then, the 2×2 matrix $G(z,t)$ can be expressed as

$$G(z,t) = \frac{\theta(t)}{2\pi}\int_{-\infty}^{\infty} dk\, \frac{e^{-ikz}}{2\sqrt{f(k)}}\left[e^{-\omega_1(k)t}\begin{pmatrix} \frac{1}{2}k^2 + 1 + W(k) - \omega_1(k) & -\omega_1(k) \\ -\frac{\delta}{2} & \frac{1}{2p}k^2 - \omega_1(k) \end{pmatrix}\right.$$

$$\left. - e^{-\omega_2(k)t}\begin{pmatrix} \frac{1}{2}k^2 + 1 + W(k) - \omega_2(k) & -\omega_2(k) \\ -\frac{\delta}{2} & \frac{1}{2p}k^2 - \omega_2(k) \end{pmatrix}\right]. \tag{4.9}$$

Unfortunately, even for $W(k)\equiv 0$, the k-integration cannot be carried out analytically.

The second step in constructing the general solution of (4.3) consists of finding a particular solution, $(u_p(z,t),m_p(z,t))$. Again by Fourier transformation one finds

$$\begin{pmatrix} u_p(z,t) \\ m_p(z,t) \end{pmatrix} = \frac{1}{2\pi}\int_{-\infty}^{\infty} dk \int_{-\infty}^{\infty} d\omega\, e^{-ikz-i\omega t} f(k,\omega) \times \begin{pmatrix} -i\omega \\ -i\omega + \frac{1}{2p}k^2 \end{pmatrix} \frac{1}{N(k,\omega)} + \begin{pmatrix} C_u \\ C_m \end{pmatrix} \quad (4.10)$$

with

$$f(k,\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dt' \int_{-\infty}^{z_0(t')} dz'\, e^{ikz'+i\omega t'} \quad (4.11)$$

which of course has to be understood as a distribution. The determinant $N(k,\omega)$ is given by

$$N(k,\omega) = \left(-i\omega + \frac{1}{2p}k^2\right) \times \left[-i\omega + \tfrac{1}{2}k^2 + 1 + W(k)\right] - i\delta\omega/2. \quad (4.12)$$

As discussed in Sec. III, one has freedom in choosing one boundary condition. In fact, the additive constants (C_u, C_m) have to fulfill only

$$\delta C_u/2 + C_m = 0. \quad (4.13)$$

Therefore we can choose one of them (e.g., C_u) freely. In the following, we consider always the physical situation of a thermodynamically stable solid ($z\to-\infty$) growing into an undercooled liquid ($z\to\infty$). We therefore choose $u_p(-\infty)=0$. This leads to

$$C_u = -\frac{1}{1+\delta/2}, \quad C_m = \frac{\delta/2}{1+\delta/2}. \quad (4.14)$$

Then,

$$u_p(-\infty)=0, \quad m_p(-\infty)=1,$$
$$u_p(\infty)=C_u, \quad m_p(\infty)=C_m \quad (4.15)$$

just as in Eq. (3.12). With this notation, we are able to write the general solution of Eqs. (4.1) and (4.2) in an analytic form. Let $\begin{pmatrix} u_0(z) \\ m_0(z) \end{pmatrix}$ be the initial condition for $t=0$ which should fulfill the same boundary conditions (4.15) as $\begin{pmatrix} u_p(z,t) \\ m_p(z,t) \end{pmatrix}$ does. Then the general solution can be expressed as

$$\begin{pmatrix} u(z,t) \\ m(z,t) \end{pmatrix} = \begin{pmatrix} u_p(z,t) \\ m_p(z,t) \end{pmatrix} + \int_{-\infty}^{\infty} dz'\, G(z-z',t) \begin{pmatrix} 1 & -1 \\ 0 & 1 \end{pmatrix} \times \begin{pmatrix} u_0(z') - u_p(z',0) \\ m_0(z') - m_p(z',0) \end{pmatrix}. \quad (4.16)$$

This can be verified by showing

$$L\begin{pmatrix} u \\ m \end{pmatrix} = L\begin{pmatrix} u_p \\ m_p \end{pmatrix} = \begin{pmatrix} 0 \\ \theta(z_0(t)-z) \end{pmatrix}$$

for $t>0$, and

$$\lim_{t\to 0}\begin{pmatrix} u(z,t) \\ m(z,t) \end{pmatrix} = \begin{pmatrix} u_0(t) \\ m_0(t) \end{pmatrix}.$$

Although Eq. (4.16) looks rather explicit, one has to remember that the $z_0(t)$ entering in $\begin{pmatrix} u_p(z,t) \\ m_p(z,t) \end{pmatrix}$ via Eqs. (4.10) and (4.11) is not known. It has to be determined from

$$m(z_0(t),t) = \tfrac{1}{2}. \quad (4.17)$$

In fact, this is an integral equation for $z_0(t)$ which can be written more explicitly as

$$\frac{1}{2} = \frac{\delta/2}{1+\delta/2} + \frac{1}{(2\pi)^2}\int_{-\infty}^{\infty} dk \int_{-\infty}^{\infty} d\omega \int_{-\infty}^{\infty} dt' \times \int_{z_0(t)-z_0(t-t')}^{\infty} dz'\, e^{-ikz'-i\omega t'} \frac{-i\omega + k^2/2p}{N(k,\omega)} \quad (4.18)$$

with the initial condition $z_0(t=0)=0$.

Let us now discuss these results (4.16) and (4.18). For physically accessible parameters, the frequencies $\omega_1(k)$ and $\omega_2(k)$ defined by (4.8) are positive for $k\neq 0$ and $\omega_1(0)>0$, $\omega_2(k)\propto k^2$, as $k\to 0$. Equation (4.9) then shows that $G(z,t)$ vanishes as $t\to\infty$. Transferred to the expression (4.16) for the general solution, this means that $\begin{pmatrix} u(z,t) \\ m(z,t) \end{pmatrix}$ approaches the particular solution $\begin{pmatrix} u_p(z,t) \\ m_p(z,t) \end{pmatrix}$ more and more closely as $t\to\infty$. This is consistent with the numerical results of Ref. 9 where it was found that a general initial condition finally approaches the steady-state solution, i.e., the steady-state solution is stable.

Let us now consider Eq. (4.18) for the interface location $z_0(t)$ in more detail. First, for symmetrical initial conditions and $u\equiv 0$, $z_0(t)\equiv 0$ and everything reduces to equilibrium. This case, where the interface merely changes its shape but does not move, can be calculated much more simply (in fact, it was studied in detail in Ref. 9) but it is irrelevant for growth processes. Next, we can recover the steady-state theory of Sec. III by making the ansatz

$$z_0(t) = vt, \quad (4.19)$$

where v has to be determined from Eq. (4.18). Then by substitution $x=z'-vt$, the t' and ω integrations in Eq. (4.18) can be done trivially and the resulting equation is just the basic Eq. (3.13) from Sec. III for the velocity v. Of course, Eq. (4.18) is also valid in the heat-diffusion governed regime $0<p<p_c$ where no steady-state solution exists. It is not clear *a priori* whether or not there is really growth, i.e., whether or not $z_0(t)$ diverges for $t\to\infty$. One can, however, surmise that crystal growth still occurs, not in a steady-state manner, but with a time-dependent velocity $v(t)\equiv dz_0(t)/dt$ and with time-dependent interfacial profiles. Little is known about this region. It would be interesting to discuss analytic and numerical properties of $v(t)$ for large t. For a numerical study, Eqs. (4.16) and (4.18) are not well suited because $z_0(t)$ is needed for negative t. We gave this expression in order to establish a link to the steady-state theory. Alternatively, one could express $u(z,t)$ and $m(z,t)$ as Laplace transforms instead of Fourier transforms to obtain a causal expression for the time development of an arbitrary initial interfacial profile that could serve as a starting point for a numerical and analytical calculation of $z_0(t)$ in the diffu-

sion-governed region. We leave this for future work.

Let us finally make a remark concerning a *conserved* order parameter m. Then the dynamics is given by making a replacement in Eq. (2.2):

$$-\frac{\Gamma}{\rho_0}\frac{\delta F}{\delta m}\bigg|_{T_0} - \gamma u \rightarrow -\nabla^2\left[-\frac{\Gamma}{\rho_0}\frac{\delta F}{\delta m}\bigg|_{T_0} - \gamma u\right]. \tag{4.20}$$

The same analysis as briefly outlined in this section can be applied. For details of the method, see again Ref. 9. The results are obtained by inserting additional factors of k^2 in many of the Fourier space expressions given. However, for a conserved order parameter, there is no steady-state solution, even for $p > p_c$, because the shape of the profile cannot be independent of time.

V. CONCLUSIONS

As this paper indicates, the results of Ref. 7 are robust: changes in the shape of the free energy do not change the conclusion that for large enough thermal diffusivity steady-state solutions for one dimensional growth no longer exist. The linearity of the equations allows one to procede much farther in the analysis in the present case, however. Although the quartic potential is undoubtedly smoother and more realistic than the intersecting parabolas model, both are evidently ad hoc. It is gratifying that two such different models share common characteristics.

The double parabola model can be generalized in a number of directions, some of which we plan to investigate in future work. Conserved as well as nonconserved order parameters can be studied, and higher order gradients in the free energy can easily be incorporated. The role of the long-range interaction $w(r)$ in physical systems needs to be looked at. It is possible to include additional order parameters, making the free energy surface an intersection of paraboloids, rather than simple parabolas. In this case, Ref. 9 showed that the dynamics could be significantly perturbed in the kinetic model in which the temperature is held fixed. It would be of interest to study this in systems which have more than one order parameter fully coupled to a temperature field varying through space.

As described in Sec. IV, one of the most interesting questions is the nature of the time-dependent solutions in the region $p < p_c$. Do the shapes of the order parameter and temperature profiles settle down at long times, with only the velocity continuing to change? Or is the non-steady-state region more complicated than this, with profiles also failing to approach fixed forms? The answers to these questions should be useful in analyzing growth in real experimental situations in which large undercoolings (approaching the isoenthalpic limit) can be achieved. Work is proceeding in these directions.[14]

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