

An exactly soluble model for interfacial kinetics

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We study an exactly soluble model for planar interfacial kinetics for both locally conserved and nonconserved order parameters, where the Landau–Ginzburg potential is approximated by two parabolas. Long-range interactions with arbitrary interaction kernels are included. In particular, the relaxation of the initial order parameter interfacial profile to its equilibrium profile is considered. Furthermore, the steady-state solution of planar interfacial growth for a nonconserved order parameter is determined. Here, the influence of a second nonconserved order parameter is also discussed.

I. INTRODUCTION

In recent years there has been increasing interest in the rates and mechanisms of interfacial kinetics for first-order phase transitions. One of the primary areas of study has been crystal growth of single-component systems from the melt.¹ Silicon has been studied experimentally by laser-induced zone melting.^{2–5} Among the striking observations of those studies are the fact that growth of the melt into a superheated solid is much faster than growth of a crystal into an undercooled liquid⁴ for the same temperature distance from the equilibrium freezing transition. In addition, faceting has been observed during growth, both in experiment and in computer simulations of silicon.⁵ Rayleigh and Raman light scattering have been used to study the width of the ice/water interface during growth, and surprisingly broad interfaces have been observed.⁶ Finally, a detailed molecular dynamics simulation of crystal growth in a Lennard-Jones system⁷ showed thermally activated behavior of the (111) interface and nonactivated behavior for the (100) interface. This study also gave information about the detailed mechanisms for growth in the two cases.

The kinetics of growth in other first-order transitions are of interest as well. Much attention has been paid to the rapid solidification of metal alloys, and the effect of growth kinetics on microstructure.⁸ Other possible applications include the dynamics of the order/disorder interface in Cu₃Au or in the three-state Potts model whose equilibrium properties were studied in Refs. 9 and 10, respectively.

Exactly soluble models for interfacial kinetics are of considerable interest, because they allow a systematic exploration of the factors that affect growth, as well as modeling of particular physical systems. The only exactly soluble model for time-dependent interface profiles of which we are aware to date is the steady-state solution of a Landau–Ginzburg φ^4 potential¹¹ which was extended and applied to crystal growth kinetics by one of us.¹² In this paper, we present a new exactly soluble model for interfacial kinetics and explore its time-dependent as well as steady-state properties.

In this model, even long-range interactions of the order parameters are included. To the best of our knowledge, this paper represents the first rigorous solution of a model for an

interface where *arbitrary* long-range interaction kernels can be treated. This makes it superior to the Sullivan model¹³ where a special (Yukawa-type) form of the interaction kernel is required. Moreover, the Sullivan model has not yet been applied to time-dependent processes. The equilibrium version of our exactly soluble model was used to investigate the influence of long-range forces on surface melting.^{14,15}

The organization of the paper is as follows: After outlining the general theory in Sec. II, we discuss the relaxation of a nonequilibrium interfacial profile to the equilibrium profile within an exactly soluble model, both for a conserved and a nonconserved order parameter in Sec. III. Then, in Sec. IV we study planar interfacial growth for a nonconserved order parameter whose steady-state solution is found exactly within our model. The influence of additional order parameters is discussed.

II. GENERAL THEORY

Consider a space- and time-dependent scalar order parameter $b(z,t)$ which may describe a planar interfacial profile, z being the coordinate perpendicular to the surface plane. We describe the time evolution of $b(z,t)$ within the Landau–Ginzburg approach^{12,16} neglecting random forces which serve only to initiate thermodynamic fluctuations:

$$\frac{\partial b}{\partial t} = -\Gamma \left(i \frac{\partial}{\partial z} \right)^n \frac{\delta F[b]}{\delta b}. \quad (2.1)$$

Here, F is the free energy functional and $\Gamma > 0$ is an Onsager coefficient which sets the microscopic time scale. Furthermore,

$$n = \begin{cases} 0 & \text{if } b \text{ is locally nonconserved} \\ 2 & \text{if } b \text{ is locally conserved} \end{cases}. \quad (2.2)$$

We assume the following form for $F[b]$:

$$F[b] = \int_{-\infty}^{\infty} dz \left\{ \frac{1}{2} g \left(\frac{\partial b(z,t)}{\partial z} \right)^2 - V[b(z,t)] \right\} \\ - \frac{1}{4} \int_{-\infty}^{\infty} dz \int_{-\infty}^{\infty} dz' w(|z-z'|) \\ \times [b(z,t) - b(z',t)]^2. \quad (2.3)$$

Here, $-V(b)$ is the free energy for a system with a spatially uniform order parameter b . At two-phase coexistence, $V(b)$ exhibits two maxima of equal height (taken to be zero) at the bulk values of the order parameter (see Fig. 1). Moreover, long-range interactions of the order parameter are taken into account via $w(z)$. This is important to describe a liquid-gas interface, for instance, b being then the mean density and $w(z)$ the laterally integrated long-ranged interparticle potential. In simple Landau-Ginzburg models, $w(z)$ is set to zero, because if $w(z)$ has a short enough range, its contribution to the free energy has the same form as the square gradient term involving g . For general $V(b)$, Eq. (2.1) is a nonlinear partial integro-differential equation which is difficult to solve. Our particular choice of $V(b)$ is two intersecting parabolas which linearize Eq. (2.1) piecewise (Fig. 1). Without loss of generality, we assume that the order parameter is zero in the first and b_s in the second phase. We are looking for solutions for the interfacial profile between the two phases. Therefore, we have the boundary conditions

$$\begin{aligned} b(z \rightarrow -\infty, t) &= 0, \\ b(z \rightarrow \infty, t) &= b_s. \end{aligned} \tag{2.4}$$

III. RELAXATION OF THE ORDER PARAMETER TO THE EQUILIBRIUM PROFILE

In this section, we study the relaxation of an initial non-equilibrium profile $b_0(z)$, given for $t = 0$, to the equilibrium profile. Note that we only consider deviations in the z direction, not in the direction parallel to the surface plane, such as the relaxation of a locally curved interface to a planar one.

Let us first define the potential $V(b)$ in the model introduced in Sec. II; it is given by two parabolas (Fig. 1),

$$V(b) = \max \left[-\frac{1}{2}\lambda b^2, -\frac{1}{2}\lambda(b - b_s)^2 \right]. \tag{3.1}$$

This then induces an external step-like force in the equations of motion¹⁵:

$$\begin{aligned} i^{-n}\Gamma^{-1} \frac{\partial b}{\partial t} - g \frac{\partial^{2+n} b}{\partial z^{2+n}} + \lambda \frac{\partial^n b}{\partial z^n} \\ + \frac{\partial^n}{\partial z^n} \int dz' w(|z - z'|) [b(z') - b(z)] \\ = b_s \lambda \frac{\partial^n}{\partial z^n} \theta [z - z_0(t)] \end{aligned} \tag{3.2}$$

where $n = 0, 2$ as in Eq. (2.2). Here $z_0(t)$ is a function that is determined from

$$b [z_0(t), t] = \frac{b_s}{2} \tag{3.3}$$

if $b(z, t)$ is a solution of Eq. (3.2). This function $z_0(t)$ equals z_0 for $t \leq 0$, with

$$b_0(z_0) = \frac{b_s}{2}. \tag{3.4}$$

We assume that Eq. (3.4) has only a single solution z_0 ; i.e., we do not consider overhanging interfacial profiles. Without loss of generality z_0 can be chosen to be zero.

The strategy is to solve Eq. (3.2) for a general $z_0(t)$ and then to determine $z_0(t)$ via Eq. (3.3). The general solution of

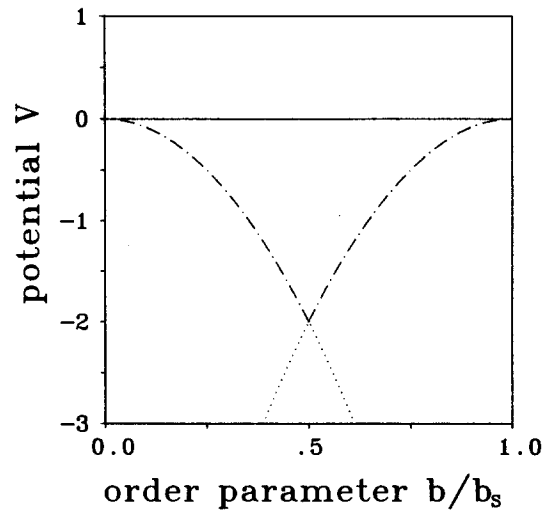


FIG. 1. Two-parabola structure of the potential $V(b)$ (dash-dotted line) in arbitrary units.

Eq. (3.2) can be obtained by Fourier transformation and is given for $t > 0$ by

$$\begin{aligned} b(z, t) &= b^P(z, t) + \int_{-\infty}^{\infty} dz' G_n(z - z', t) \\ &\quad \times [b_0(z') - b^P(z', 0)], \end{aligned} \tag{3.5}$$

where $b_0(z)$ is the initial profile for $t = 0$ and

$$G_n(z, t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dk e^{-ikz} e^{-[gk^2 + \lambda + W(k)]k^n \Gamma t} \tag{3.6}$$

is the Green's function of the generalized diffusion equation (3.2). Furthermore, $b^P(z, t)$ is given by

$$\begin{aligned} b^P(z, t) &= \frac{b_s \lambda \Gamma}{2\pi} \int_{-\infty}^t dt' \int_{-\infty}^{z - z_0(t')} dz' \\ &\quad \times \int_{-\infty}^{\infty} dk k^n e^{-ikz'} e^{-k^n(t-t')\Gamma [gk^2 + \lambda + W(k)]}. \end{aligned} \tag{3.7}$$

Finally, $W(k)$ is

$$W(k) = \sqrt{2\pi} [\tilde{w}(k) - \tilde{w}(0)], \tag{3.8}$$

where \sim denotes the Fourier transform.

Because $z_0(t)$ enters Eq. (3.7) nonlocally, Eq. (3.3) which determines $z_0(t)$ is a nonlinear integral equation. We have thus reduced the nonlinear (piecewise linear) partial integro-differential equation to an ordinary integral equation. In general, the Volterra-type equation (3.3) cannot be solved analytically. However, there is an interesting simple case where a trivial solution $z_0(t)$ of Eq. (3.3) can be found. If the initial profile is an odd function about $z = 0$, $b = b_s/2$:

$$b_0(z) - \frac{b_s}{2} = -b_0(-z) + \frac{b_s}{2}, \tag{3.9}$$

then by symmetry it will remain an odd function at all times. We can then set $z_0(t)$ to zero, and Eq. (3.7) simplifies to the static solution

$$b^P(z,t) \equiv b^P(z) = \frac{\lambda b_s}{2\pi} \int_{-\infty}^z dz' \times \int_{-\infty}^{\infty} dk \frac{e^{-ikz'}}{gk^2 + \lambda + W(k)}. \quad (3.10)$$

For a step-function initial profile $b_0(z) = b_s \theta(z)$ the relaxation of the interfacial profile to $b^P(z)$ is shown in Figs. 2 and 3 for both nonconserved ($n=0$) and conserved ($n=2$) order parameters. Remarkably, for a conserved order parameter a nonmonotonic profile $b(z)$ is generated during the relaxation like a damped traveling shock wave.

Within the exact solution (3.5), Eq. (3.10) we can also study the long-time behavior if the initial profile is odd about $z=0$, see Eq. (3.9). Then, for large t , the interface profile approaches $b^P(z)$ as

$$b(z,t) - b^P(z) \sim \begin{cases} [t^{-3/2} + \mathcal{O}(t^{-5/2})] e^{-\lambda \Gamma t} & \text{for } n=0 \\ t^{-3/2} + \mathcal{O}(t^{-5/2}) & \text{for } n=2 \end{cases}. \quad (3.11)$$

So, as expected physically, the profile decays much faster (exponentially) for a nonconserved order parameter than for a conserved one. In the latter case the conservation reduces the decay behavior to a power law with universal exponent $-3/2$.

IV. PLANAR INTERFACE GROWTH FOR A NONCONSERVED ORDER PARAMETER

In this section, we consider a different situation where one of the two phases is metastable. A planar interface which separates these two phases will then move into the metastable phase; i.e., the stable phase will grow at the expense of the metastable one. Such a situation can be investigated with a potential $V(b)$ that is sketched in Fig. 4. As in Sec. III, the

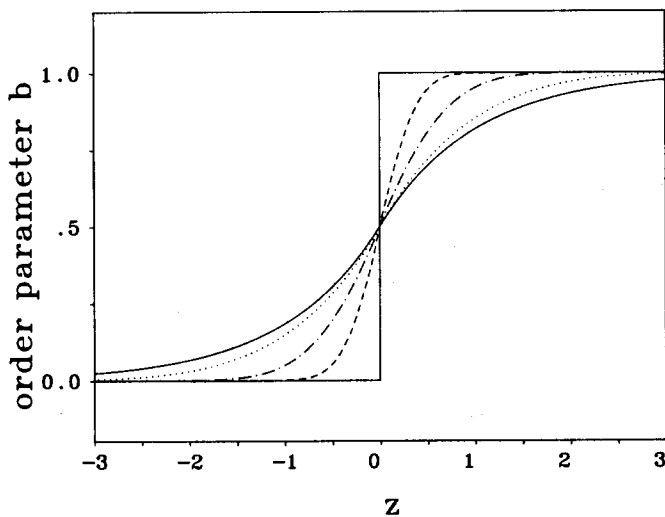


FIG. 2. Relaxation of a stepfunction initial ($t=0$) profile $b(z)$ to its equilibrium value ($t=\infty$) for a nonconserved order parameter. The units are arbitrary; we chose $w(z)=0$ and $g=\lambda=\Gamma=b_s=1$. The profiles for five different times are shown: $t=0$ (solid line, step function), $t=0.05$ (broken line), $t=0.2$ (dash-dotted line), $t=0.75$ (dotted line), and $t=\infty$ (solid line).

general solution for the time development of an order parameter profile yields a Volterra-type integral equation for $z_0(t)$, where z_0 is the position where $b(z,t)$ lies on the intersection line of the parabolas of $V(b)$. A rich variety of solutions may occur both for conserved and nonconserved order parameters. We restrict ourselves to steady-state solutions, where the interface moves with a constant velocity v , but does not change its shape. As is physically clear, such solutions with a fixed interface shape are only expected for a nonconserved order parameter. If the order parameter is conserved, a moving interface cannot retain its shape.

Let us first consider a single nonconserved order parameter and discuss the properties of the steady-state solution with the exactly soluble model. Then we also study the influence of a second nonconserved order parameter.

A. A single order parameter

Because the first phase is now metastable, we now choose the potential $V(b)$ to be a combination of two parabolas which differ by an amount ϵ in their height. ϵ is proportional to the temperature difference from the coexistence temperature of the two phases. That is (see Fig. 4),

$$V(b) = \max[-\frac{1}{2}\lambda b^2 - \epsilon, -\frac{1}{2}\lambda(b - b_s)^2]. \quad (4.1)$$

The intersection of the parabolas is at

$$b = \frac{b_s}{2} - \frac{\epsilon}{\lambda b_s}. \quad (4.2)$$

Because we are looking for a steady solution, we connect the variables z and t via a new variable $x \equiv z + vt$, v being the interface velocity. This reduces the partial integrodifferential equation of motion (2.1) to an ordinary one. Prescribing that the interface position is at $x=0$, the nonlinearity can be transferred into a stepfunction external force. For given v , we find a solution, and by inserting it into Eq. (4.2), we

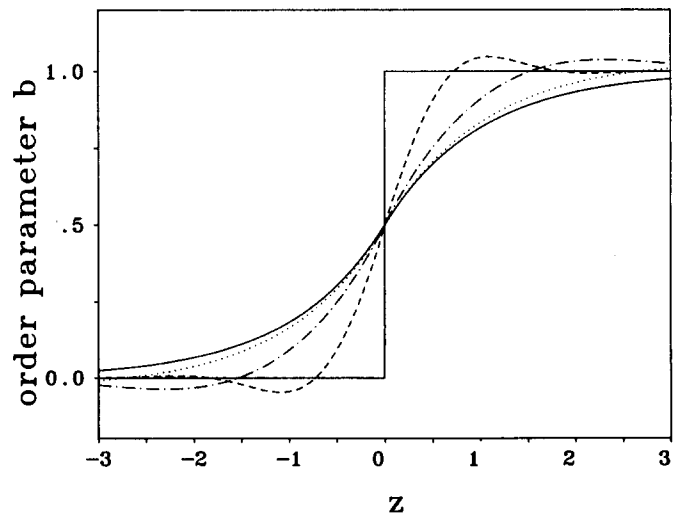


FIG. 3. Same as Fig. 2 for a conserved order parameter. The parameters are chosen as in Fig. 2. The different times are $t=0$ (solid line), $t=0.01$ (broken line), $t=0.2$ (dash-dotted line), $t=2$ (dotted line), and $t=\infty$ (solid line).

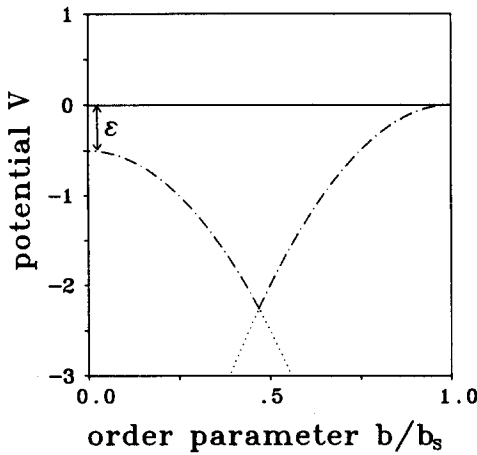


FIG. 4. Same as Fig. 1, now with one phase metastable. The distance from coexistence is denoted by ϵ .

obtain a relation $v(\epsilon)$. Clearly, $v(\epsilon \rightarrow 0) = 0$. Furthermore $v(\epsilon)$ should be monotonic in ϵ .

The explicit result for the steady-state solution is

$$\bar{b}(x) = \frac{\lambda b_s}{2\pi} \int_{-\infty}^x dy \int_{-\infty}^{\infty} dk \frac{e^{-iky}}{gk^2 - ikv\Gamma^{-1} + \lambda + W(k)} \quad (4.3)$$

with $W(k)$ from Eq. (3.8) and $v(\epsilon)$ obtained by inserting $\bar{b}(x=0)$ into Eq. (4.2). This function is illustrated in Fig. 5. For symmetry reasons, $v(\epsilon)$ is an odd function. For small ϵ and v , we find the expansion

$$\epsilon = \bar{A}v + \bar{C}v^3 + \mathcal{O}(v^5) \quad (4.4)$$

with

$$\bar{A} = \frac{\lambda^2 b_s^2 I_0}{2\pi\Gamma}, \quad \bar{C} = \bar{A}I_2 / (I_0\Gamma^2), \quad (4.5)$$

and

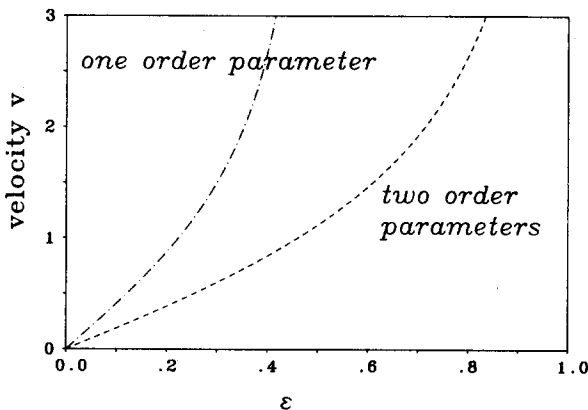


FIG. 5. Interface velocity v as a function of ϵ for both one and two nonconserved order parameters in arbitrary units. We chose $w(z) = 0$ and $\lambda = g_0 = g_1 = b_{0s} = \Gamma_0 = \Gamma_1 = \mu_0 = 1, \mu_1 = 2$ for the two order parameter case. For one order parameter the parameters are as in Fig. 2.

$$I_m = \int_{-\infty}^{\infty} dk \frac{k^m}{[gk^2 + \lambda + W(k)]^{2+m}} \quad (4.6)$$

B. Two order parameters

The models (2.1) and (2.3) can be extended in a straightforward fashion to additional order parameters. Let $\mathbf{b} = (b_0, b_1)$ denote the two order parameters. Then, Eq. (2.1) is generalized to

$$\frac{\partial b_j}{\partial t} = -\Gamma_j \frac{\delta F[\mathbf{b}]}{\delta b_j}, \quad j = 0, 1, \quad (4.7)$$

In this section, we take $F[\mathbf{b}]$ to be

$$F[\mathbf{b}] = \int_{-\infty}^{\infty} dz \left\{ \frac{1}{2} g_0 \left(\frac{\partial b_0(z,t)}{\partial z} \right)^2 + \frac{1}{2} g_1 \left(\frac{\partial b_1(z,t)}{\partial z} \right)^2 - V[\mathbf{b}(z)] \right\} - \frac{1}{4} \int_{-\infty}^{\infty} dz \int_{-\infty}^{\infty} dz' w(|z-z'|) [b_0(z) - b_0(z')]^2. \quad (4.8)$$

Note that only b_0 is coupled via $w(z)$. As a physical example for Eq. (4.8), we mention applications to the liquid–solid interface.^{14,15} The boundary conditions are now

$$\mathbf{b}(z \rightarrow -\infty, t) = 0, \quad \mathbf{b}(z \rightarrow +\infty, t) = \mathbf{b}_s. \quad (4.9)$$

The function $V(\mathbf{b})$ again is approximated by two parabolooids:

$$V(\mathbf{b}) = \max \left[-\frac{\lambda}{2} b_0^2 - \frac{\mu_0}{2} b_1^2 - \epsilon, -\frac{\lambda}{2} (b_0 - b_{0s})^2 - \frac{\mu_1}{2} (b_1 - b_{1s})^2 \right]. \quad (4.10)$$

Note that the curvatures μ_0, μ_1 in the b_1 direction are not equal in the two phases. However, because b_1 is not coupled by $w(z)$, Eqs. (4.7) are piecewise linear differential equations. Transforming to $x \equiv z + vt$, $b_0(x)$ is given by Eq. (4.3), and furthermore

$$b_1(x) = \begin{cases} b_{1s} e^{\omega_1 x} / (1 + \omega_1 / \omega_2) & \text{for } x < 0 \\ b_{1s} [1 - \omega_1 e^{-\omega_2 x} / (\omega_1 + \omega_2)] & \text{for } x > 0 \end{cases} \quad (4.11)$$

with

$$\omega_j = -(-1)^j v / (2g_j \Gamma_j) + \sqrt{[v / (2g_j \Gamma_j)]^2 + \mu_j / g_j}, \quad j = 1, 2. \quad (4.12)$$

Inserting $\mathbf{b}(x=0)$ into the intersection line of the parabolooids,

$$2\lambda b_{0s} b_0 = \lambda b_{0s}^2 + \mu_1 (b_1 - b_{1s})^2 - \mu_0 b_1^2 - 2\epsilon \quad (4.13)$$

yields the function $v(\epsilon)$. Now, because $\mu_0 \neq \mu_1$, $v(\epsilon)$ is no longer an odd function. This is also shown in Fig. 5. With $s_j \equiv \sqrt{\mu_j}$ and $r = \sqrt{g_1}$ the expansion

$$\epsilon = \bar{A}v + \bar{B}v^2 + \bar{C}v^3 + \mathcal{O}(v^4) \quad (4.14)$$

now has the coefficients

$$\bar{A} = \lambda^2 b_{0s}^2 I_0 / (2\pi\Gamma_0) + b_{1s}^2 s_0 s_1 / [2r\Gamma_1(s_0 + s_1)], \quad \bar{B} = b_{1s}^2 (s_1 - s_0) / [4r\Gamma_1^2 (s_1 + s_0)], \quad (4.15)$$

$$\bar{C} = \lambda^2 b_{0s}^2 I_2 / (2\pi \Gamma_0^3) - b_{1s}^2 (2\mu_0 s_1 + 2\mu_1 s_0 - s_0^3 - s_1^3) / [16r^3 \Gamma_1^3 s_0 s_1 (s_0 + s_1)^2].$$

I_n is given by Eq. (4.6) if $g \equiv g_0$. As is seen from Eq. (4.15) or from Fig. 5, the existence of a second order parameter reduces the velocity for a given ϵ .

V. CONCLUSIONS

We have discussed interfacial kinetics within an exactly soluble model. The relaxation of a nonequilibrium interfacial profile to the equilibrium profile was studied both for a nonconserved and a conserved order parameter. It turned out that a nonconserved OP profile decays much faster in time (namely exponentially) than a conserved OP profile which decays as $t^{-3/2}$ for long times. In the latter case, damped oscillations in the profile may occur. Furthermore, we gave the steady-state solution for planar interfacial growth of a nonconserved order parameter if one phase is metastable. The existence of further order parameters reduces the velocity of the steady-state solution. Because the analysis of our exactly soluble model is rather general, a great number of related questions can now be addressed within this model.

As a first application, we mention that a slightly more general equation of motion for a locally conserved order parameter is¹⁷

$$\frac{\partial b}{\partial t} = -\Gamma \left[1 - \exp\left(\frac{l^2}{2} \frac{\partial^2}{\partial z^2}\right) \right] \frac{\delta F[b]}{\delta b}, \quad (5.1)$$

l being a "diffusion length." This is to be contrasted with Eq. (2.1) which follows from Eq. (5.1) if the exponential is expanded to first order. The same analysis as in Sec. III is possible and Eqs. (3.5)–(3.7) remain valid if one makes the following replacement:

$$\Gamma k^n \equiv \Gamma k^2 \rightarrow \Gamma \left[1 - \exp\left(-\frac{l^2}{2} k^2\right) \right]. \quad (5.2)$$

In some first-order phase transitions, both conserved and nonconserved order parameters play a role. An example is the crystallization of a liquid, where the (nonconserved) crystalline structure and (conserved) average density are coupled variables. The role of the density change on freezing was ignored in Ref. 12, on the grounds that its magnitude is small so it should have little effect on dynamics. On the other hand, Richards¹⁸ has argued that the density change may play a crucial role, especially in accounting for the asymmetry in the temperature dependence of the melting and freezing rates of silicon described in Ref. 4. It will be of interest to extend the approach in this paper by coupling a primary nonconserved variable to a conserved variable to study the effect of average density, and to investigate the asymmetry in freezing and melting from a theoretical point of view.

The theory outlined in this paper assumed that the interfacial dynamics is governed entirely by the time evolution of the order parameter, and that the temperature can be considered to be a constant. In other words, the heat is assumed to be removed rapidly enough that no temperature change occurs as the latent heat of the phase transition appears at the interface. A possible extension would be to couple the order parameter dynamics to an additional equation for the local

temperature, one that includes the release of latent heat and its diffusion. Such coupled equations have been studied in Refs. 19 and 20, and can show quite different velocity selection from the simpler equations that ignore temperature variation through the system.

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