

Critical Behavior of Crystal Growth Velocity.

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Abstract. – Within a phase-field model that couples a nonconserved order parameter to the temperature field, we study the crystal growth velocity v in a supercooled liquid as a function of the undercooling Δ . The velocity shows critical behavior in Δ depending on the ratio p of effective diffusion constants and on δ , which measures the coupling between the order parameter and the temperature field. As Δ becomes smaller, there is a transition from steady-state growth to a diffusive regime. At the phase boundary, v remains nonzero for $p > p_c$; otherwise, it vanishes as $(\Delta - \Delta_c)^\nu$ with $\nu = 1$ for $p < p_c$, $\nu = 1/2$ for $p = p_c$, and $\nu = 1/3$ for $p = p_c$ and $\delta = \delta_c$, which corresponds to a critical point $(\Delta_c, p_c, \delta_c)$ in the (Δ, p, δ) parameter space. Typical experimental systems have $p < p_c$; however, if impurity concentration gradients dominate over temperature variations, p is much larger and δ may be tuned by varying the overall impurity concentration.

Recently, several unusual features of the phase-field model of solidification have been discovered [1, 2]. In this model [3-5], a nonconserved order parameter is coupled to a temperature field, thus taking into account not only finite interface width and nonequilibrium kinetics, but also the release and subsequent diffusion of latent heat. The usual models of solidification have tended to focus on the former [6] or on the latter [7] aspects.

The phase-field model is defined in terms of a nonconserved order parameter $m(z, t)$ and a dimensionless undercooling $u(z, t)$, which is given by $u \equiv (T - T_0)/(L/c_p)$, where $T(z, t)$ is the temperature field, T_0 is the solid-liquid coexistence temperature, c_p the specific heat, and L the latent heat of transition. The scaled equations of motion for m and u in a one-dimensional geometry are

$$u_t = \frac{1}{2p} u_{zz} + m_t, \quad (1a)$$

$$m_t = \frac{1}{2} m_{zz} - \frac{\partial f}{\partial m} - \frac{\delta u}{2}, \quad (1b)$$

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where space and time are scaled by $l_m = K\sqrt{2/\lambda}$, $\tau_m = 1/\lambda\Gamma$, K being a microscopic correlation length of the order parameter m , λ a dimensionless scale of the bulk free-energy density, and Γ the kinetic relaxation rate for m . The two dimensionless control parameters in eqs. (1) are $p \equiv K^2\Gamma/\alpha$, which is the ratio of order-parameter diffusivity ($K^2\Gamma$) to thermal diffusivity (α), and $\delta \equiv (2/\lambda)(L/(k_B T_0))(L/(c_p T_0))$, which measures the coupling between m and u . For the free-energy density $f(m)$ at T_0 , we choose a piecewise parabolic potential [8]:

$$f(m) = \frac{1}{2} \min[m^2, (m-1)^2]. \quad (2)$$

The order parameter m is 0 in the liquid and 1 in the solid. This form of $f(m)$ makes the equations of motion piecewise linear, but preserves the essential physics.

We shall focus on steady-state solutions of the form $m(z, t) = m(z - vt)$, $u(z, t) = u(z - vt)$, where v is the solid-liquid interface velocity, which must be determined. The original interest of the phase-field model for solidification arose when it was shown that, for unit undercooling, one could find steady-state solutions for which the front velocity was uniquely determined [3, 4]. This is in contrast to the analogous situation in standard diffusive models, where the velocity is undetermined.

This result was for fixed control parameters δ and p . Schofield *et al.* then found, at the same «unit» undercooling, that for a sufficiently large value of the thermal diffusivity (*i.e.* a sufficiently small value of p), there is no steady-state solution at all [1, 2]. Instead, the interface velocity decays as $t^{-\nu}$, with $\nu \approx 0.2$ [9]. Note that the value of this exponent is different from that expected from dimensional analysis of diffusion-dominated growth ($\nu = 0.5$).

In this paper, we elucidate the conditions under which steady states exist, for arbitrary material constants p and δ and for *arbitrary* undercooling Δ . The motivation is twofold: first, diffusion models that incorporate kinetic undercooling predict [10, 11] that below unit undercooling of the liquid, the steady-state velocity should grow as $v \propto (\Delta - 1)$, and it is interesting to know how this prediction fares in a more detailed model. In fact, it turns out that the behavior is more subtle: we shall find a critical point $(\Delta_c, p_c, \delta_c)$. As one varies Δ , there can be discontinuities and associated hysteresis in v . Second, whereas p and δ are fixed material parameters, Δ can be varied in an experiment. Thus, critical behavior in Δ is directly observable in growth experiments.

To begin, we define carefully the undercooling and the boundary conditions to eqs. (1) by generalizing the procedure of ref. [1]. We consider a solid front that starts at $z = -\infty$ and invades a liquid phase extending out to $z = +\infty$. In a reference frame moving at a velocity v , eq. (1a) becomes

$$u_{zz} + (2pv)u_z - (2pv)m_z = 0. \quad (3)$$

This can be integrated twice to give

$$\begin{aligned} u(z) &= C + 2pv \int_{-\infty}^z dz' \exp[-2pv(z-z')] m(z') = \\ &= C + m(z) - \int_{-\infty}^z dz' \exp[-2pv(z-z')] \frac{\partial m(z')}{\partial z'}, \end{aligned} \quad (4)$$

where the second step is via an integration by parts, C is an integration constant, and $m(x)$ is treated formally as a source term for an inhomogeneous equation for u . Since $\partial m(z)/\partial z = 0$ at $z = \pm\infty$, we have the boundary conditions

$$u(+\infty) - m(+\infty) = u(-\infty) - m(-\infty) = C. \quad (5a)$$

In addition, we require that the order parameter relax to its local equilibrium value at $z = \pm \infty$. Referring to eq. (2), we have on the solid side ($z = -\infty$)

$$\left. \frac{df}{dm} \right|_{m(z=-\infty)} = m(-\infty) - 1 = -\frac{\delta}{2} u(-\infty), \tag{5b}$$

while on the liquid side ($z = +\infty$)

$$\left. \frac{df}{dm} \right|_{m(z=+\infty)} = m(+\infty) = -\frac{\delta}{2} u(+\infty). \tag{5c}$$

Taken together, eqs. (5) highly constrain the form of the boundary conditions. Indeed, if we hold the liquid at an undercooling Δ , *i.e.* if $u(+\infty) = -\Delta$, then eqs. (5) imply that

$$u(-\infty) = \frac{1}{1 + \delta/2} - \Delta, \quad m(-\infty) = \Delta \frac{\delta}{2} + \frac{1}{1 + \delta/2}, \quad m(+\infty) = \Delta \frac{\delta}{2}. \tag{6}$$

For $\Delta = \Delta_c \equiv 1/(1 + \delta/2)$, we recover the boundary conditions in [2]. They correspond to unit undercooling in the pure diffusion models, since $\delta = 0$ in the latter. For unit undercooling, the latent heat is just enough to reheat the solidified matter back up to the coexistence temperature. If $\Delta > \Delta_c$, the solid will be slightly undercooled far away from the interface, as is implicit in eqs. (5). If $\Delta < \Delta_c$, the solid is overheated and the liquid supercooled, so this is a globally metastable situation; any steady-state solution is dynamically unstable [12]. In fact, we shall consider below situations where $\Delta \leq \Delta_c$, which corresponds to a slightly superheated solid propagating into a strongly undercooled liquid. See the discussion below.

In [2], the above model was solved at $\Delta = \Delta_c$ by Fourier transformation. The calculations are similar here⁽¹⁾, and we find that the steady-state velocity obeys the equation

$$\frac{1}{2} - \frac{\Delta\delta}{2} = 2 \sum_{\text{Re } x_j < 0} \frac{x_j + 2pv}{x_j \prod_{i \neq j} (x_j - x_i)}, \tag{7}$$

where $\{x_j, j = 1, 2, 3\}$ are the complex roots of the cubic equation

$$x^3 + 2v(p + 1)x^2 - 2(1 - 2pv^2)x - 2pv(2 + \delta) = 0. \tag{8}$$

In the limit $p \rightarrow \infty$, the velocity reaches a maximum:

$$v_{\text{max}} = \frac{A}{\sqrt{2 + \delta + 2A}}, \tag{9}$$

where $A = 2/(1 - \Delta\delta) - 2 - \delta$. The velocity v_{max} is a monotonically increasing function of Δ .

The transition from a steady-state regime to a diffusion-dominated regime, where the interface slows down, can be found numerically by seeing where eq. (7) has no solutions. Since at the point where the steady-state solution disappears, v is either zero or small, we can expand in v :

$$0 = \frac{\delta}{4}(\Delta - \Delta_c) + \frac{3\sqrt{2}\delta}{16}(p - p_c)v - E(p, \delta)v^2 - G(p, \delta)v^3 + O(v^4), \tag{10}$$

⁽¹⁾ Compare eqs. (3.19) and (3.20) in ref. [2].

with $p_c = p_c(\delta) \equiv 2/(3\delta)$ and where $E(p, \delta)$ is given by

$$E(p, \delta) = -\frac{pd}{c^2} + \frac{1}{2} \left(\frac{1}{4} - \frac{p}{c} \right) (b + (a+c)^2) + \frac{p}{4} (2a+c),$$

where

$$a = \frac{p\delta}{2} - 1, \quad b = 3a^2 + 4a(p+1) + 4p, \quad c = p(2+\delta), \quad \text{and} \quad d = \frac{-c^3}{2} + (p+1)c^2 - 2pc.$$

When $p = p_c$, $E(p, \delta)$ is a continuous function that is positive for $0 \leq \delta < 4/3 \equiv \delta_c$ but negative for $\delta > \delta_c$. In particular, one finds

$$E(p_c(\delta_c), \delta) = E\left(\frac{1}{2}, \delta\right) = -\frac{1}{8}(\delta - \delta_c) + O[(\delta - \delta_c)^2]. \quad (11)$$

Furthermore, the coefficient G of the stabilizing cubic term is nonzero here: $G(p_c, \delta_c) = 0.06$.

Equations (10), (11) are the central result of this paper. Although the algebra is complicated, the results have an easily understood interpretation: there is a point $(\Delta_c, p_c, \delta_c) = (3/5, 1/2, 4/3)$ where the first three coefficients in the small- v expansion vanish simultaneously. This is completely analogous to the Landau theory of second-order phase transitions [13] if one identifies v with the order parameter, $-p$ with temperature, and $\Delta - \Delta_c$ with an external field. The quadratic coefficient E in eq. (10) vanishes in the usual Landau theory of the second-order liquid-gas transition but is nonzero for second-order phase transitions in liquid crystals. In terms of this analogy, the point $(\Delta_c, p_c, \delta_c)$ may be called a critical point.

Let us now derive the different scaling laws implicit in eq. (10). If the material parameters are set to p_c and δ_c , the boundary between the steady-state and diffusion-dominated regimes is given by

$$v = \sqrt[3]{\delta_c/4G(p_c, \delta_c)} (\Delta - \Delta_c)^{1/3} \approx 1.7(\Delta - \Delta_c)^{1/3}.$$

If $\delta < \delta_c$, there is a square-root decay for $p = p_c \equiv 2/(3\delta)$ given by $v \approx \sqrt{\delta/4E(p_c, \delta)} (\Delta - \Delta_c)^{1/2}$. However, if $p < p_c$, we have a linear law $v \approx [4/3\sqrt{2}(p - p_c)](\Delta - \Delta_c)$ for $\Delta > \Delta_c$. For $p > p_c$, the phase boundary occurs at a different undercooling $\bar{\Delta}_c$ that is smaller than Δ_c . If $p \approx p_c$, one finds $\Delta_c - \bar{\Delta}_c \approx (9/512)(\delta^2/E^2(p_c, \delta))(p - p_c)^2$. For $\Delta = \bar{\Delta}_c$, the velocity has a finite value $v_c \neq 0$. Near Δ_c , one has $v_c \approx \sqrt{\delta/2E(p_c, \delta)}(\Delta_c - \bar{\Delta}_c)^{1/2}$. In fig. 1, the velocity v is plotted against Δ . The curves are based on numerical solution of eq. (7) for three different values of p/p_c . The critical velocity $v_c(\bar{\Delta}_c)$ is clearly indicated (dashed line). Note that there are two solutions (with differing velocities v) in the region $\bar{\Delta}_c < \Delta < \Delta_c$ for $p > p_c$. The lower branch (short-dashed line in fig. 1) corresponds to a front that travels faster as the undercooling is reduced. Physically, this seems unlikely, and the solution is presumably unstable. See [14] for a similar situation. Indeed, since in the regime $\bar{\Delta}_c < \Delta < \Delta_c$ the system is globally metastable, any steady-state solution—including the upper branch—is dynamically unstable.

In order to clarify the crystal growth dynamics in this globally metastable regime, we have solved the full time-dependent equations (1) starting from a finite solid germ [9]. For $t = 0$, the boundary conditions for m and u were «liquid» for $z \rightarrow \pm \infty$ and «solid» for $z = 0$, in accordance with eqs. (5) and (6). The order parameter and temperature profiles were then followed numerically for very large times. These calculations strongly support the following picture: after an initial rapid decay to a quasi-steady-state profile, the crystal-liquid interface grows at a constant velocity corresponding to that of the upper branch in the

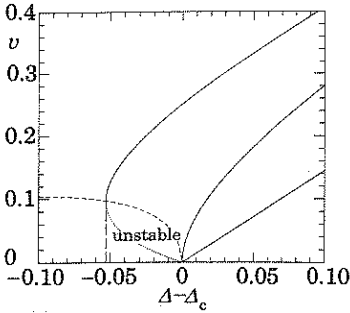


Fig. 1.

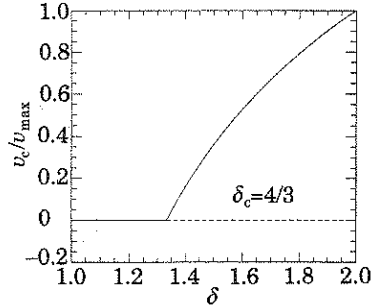


Fig. 2.

(11) Fig. 1. - Velocity v vs. undercooling Δ relative to Δ_c , for $\delta = 0.5$, which is far below the critical value ($\delta = \delta_c = 4/3$). Solid curves give the velocity for $p/p_c = 2, 1$ and 0.5 . For $p/p_c = 2$ and $\Delta < \Delta_c$, there are two solutions: an unstable lower branch (dotted line) and a «quasi-stable» (though globally metastable) upper branch (solid line). (See text.) The long-dashed vertical line denotes the jump in v for $\Delta = \bar{\Delta}_c$. The dashed line gives the critical velocity v_c as a function of $\bar{\Delta}_c$.

Fig. 2. - Velocity as a function of δ for $\Delta = \Delta_c$ and $p = p_c$.

unstable region of fig. 1. For very long times, the front slows down. Both the «extra» heat from solidification and that from the superheated solid diffuse into the liquid. Thus, by exchanging heat through its interface, the system goes from a constant-velocity, globally metastable state to a state where the velocity decays. However, since this final relaxation is slow, it is conceivable that in real systems such globally metastable solutions occur as hysteresis effects if Δ is made slightly smaller than Δ_c .

Next, we consider a very large coupling δ between the temperature and the order parameter field. For $p = p_c$ and $\Delta = \Delta_c$, the interface velocity v_c is shown as a function of δ in fig. 2. At $\delta = \delta_c$ it becomes nonzero. Although for such a large coupling δ , other order parameters may become relevant and the growth behavior more subtle, one can hope that—at least qualitatively—the velocity-undercooling scaling laws discussed above continue to hold.

For succinonitrile, one can estimate [1] $\delta \approx 0.11$. Using experimental estimates of the interface velocity per unit undercooling ($\zeta \approx 20$ cm/s/°C) [15], we have $p \approx 0.1$ and $p/p_c \approx 0.01$. We have also examined the materials parameters for a number of other substances, including metals, rare gases, and liquid-crystal transitions. Although the coupling δ can be comparable or even exceed δ_c , the ratio p/p_c seems to range from 0.1 for strongly first-order transitions to as little as 10^{-6} for weak liquid-crystalline transitions. Thus, generically we can set $p \approx 0$ in the above discussion, which implies a linear velocity-undercooling law for greater than critical undercoolings. Still, there may exist substances with unusually rapid kinetics, for which the effects described in this paper are relevant. Good candidates should have very close solid and liquid densities, to minimize the distance matter must be transported during the phase transition.

Finally, the most promising experimental situation may well be one in which impurity diffusion dominates over latent heat diffusion. (Temperature variations can be essentially eliminated by using very thin samples, where the surrounding glass plates conduct most of the latent heat away.) Because impurities usually have different solubilities in the solid and liquid phases (as reflected in the equilibrium partition coefficient $k \equiv c_{\text{solid}}/c_{\text{liquid}}$), there will be a jump in concentration of impurities across the interface. As Langer has discussed [16], the equations of motion for an impurity-dominated system are formally identical to those of the thermal case, if one makes the following correspondences: temperature $T \rightarrow$ chemical

potential μ , entropy density s_L and $s_S \rightarrow$ impurity concentration c_L and c_S ,

$$u = \frac{T - T_0}{L/c_p} \rightarrow \frac{\mu}{(\partial\mu/\partial c) \Delta c} \approx \frac{\mu T_m}{T' L}, \quad p \rightarrow \frac{\xi_0^2 \Gamma}{D},$$

and the coupling

$$\delta \rightarrow \frac{2}{\lambda} L \left(\frac{T_m - T}{T_m} \right) (1 - k).$$

Here, $T' \equiv dT/dc$ is the slope of the liquidus line on the temperature-concentration phase diagram, $\Delta c = \Delta c(T) = c_L - c_S$ is the temperature-dependent miscibility gap, and D is the chemical diffusivity of impurities.

In the liquid phase, $D/\alpha \leq 10^{-2}$, implying that p is about 100 times larger in the impurity case. Of course, although the thermal diffusivity α does not vary much between solid and liquid, D does, and this should be taken into account. The coupling constant δ is of particular interest, since it is now a function of temperature. The experiment is at fixed T (usually near $T_m - T' c_\infty$, where c_∞ is the average impurity concentration of the whole sample). Since concentration can be varied easily by a factor of 100, so may the range of accessible δ 's. For succinonitrile doped with acetone [17], we estimate $0.003 < \delta < 0.3$ for $0.1 \text{ mol\%} < c < < 10 \text{ mol\%}$ acetone. Since now $p \approx 10$, we expect $0.05 < (p/p_c) < 5$. It should therefore be possible to study the crossover between diffusive and kinetic motion, as well as the various scaling regimes discussed above.

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