Planar Solidification from Undercooled Melt: An Approximation of a Dilute Binary Alloy for a Phase-field Model

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Abstract. Planar solidification from an undercooled melt has been considered using the phase-field model. The solute and the phase fields have been found in the limit of small impurity concentration. These solutions in the limit of vanishing velocity of the interface motion give the equilibrium partition coefficient and the liquidus slope. Asymptotic expansions for the solute and for the phase fields, and the relation between the diffusive speed and the parameters of the phase field model have been found at high growth velocity. A comparison with numerical calculations is presented.

1 Introduction

Classical macroscopic models of solidification are based on the assumption that the interface between regions of different phases have zero thickness [1]. Sharp-interface descriptions require the introduction of separately derived nonequilibrium models for the behavior of the interfacial temperature and of the solute concentrations. In contrast to the sharp-interface models, the phase-field models [2,3] describe the bulk phases as well as the interface, i.e. these models treat the system as a whole and eliminate the need to specify the interfacial conditions separately. In phase-fields models, equilibrium behavior is recovered at low growth velocities and nonequilibrium effects naturally emerge at high growth velocities. From a computational point of view, the advantage of the phase-field formulation is that the interface is not tracked but is given implicitly by the value of the phase-field variable. However, theoretical analysis solutions were obtained by matching of separately derived “inner” (near the interface) and “outer” (far from the interface) solutions in an intermediate region [4,5]. In the work [6], phase-fields and solute profiles have been obtained without using the multiply-variable expansion, which leads to “inner” and “outer” solutions, but the profiles were obtained from a simplified set of equations in which the interface kinetics was eliminated.

In this work an analytical solution of the phase-field model for planar solidification from an undercooled melt as an expansion in terms of the solute concentration far from the interface is presented. This solution is valid for the bulk phases as well as for the interface and includes the interface kinetics. To verify the expansion, numerical simulations of the problem were carried out.
2 The Model

Let us consider the motion of a planar solid-liquid interface during the solidification of a binary alloy. The governing equations for the phase-field $\phi(x,t)$ and for the solute concentration $c(x,t)$ are given by the following set of equations \[1\]

\[
\frac{\partial \phi}{\partial t} = M_1 \left( \epsilon^2 \frac{\partial^2 \phi}{\partial x^2} - \frac{\partial f}{\partial \phi} \right), \quad \frac{\partial c}{\partial t} = \frac{\partial}{\partial x} M_2 c (1 - c) \frac{\partial f}{\partial \phi},
\]

which satisfy the conservation of solute and which have been derived under the assumption that the total free-energy decreases monotonically in time. The parameters $M_1$, $M_2$, and $\epsilon$ are related to the growth kinetics, to the diffusion coefficient, and to the surface energy respectively.

In the approach of ideal solution, the free-energy density $f(\phi,c,T)$ at a temperature $T$ is given by \[2\]

\[
f(\phi,c,T) = cf_B(\phi,T) + (1 - c)f_A(\phi,T) + \frac{RT}{v_m} [c \ln c + (1 - c) \ln(1 - c)],
\]

where $R$ is the universal gas constant, $v_m$ is the molar volume, which is assumed to be constant. Free-energy densities of the pure materials $A$ and $B$ are assumed to be of the form \[3\]

\[
f_i(\phi,T) = W_i \int_0^\phi p(p-1) \left( p - \frac{1}{2} - \beta_i(T) \right) dp = \frac{W_i}{4} g(\phi) + \frac{W_i\beta_i(T)}{6} p(\phi)
\]

where

\[
g(\phi) = \phi^4 - 2\phi^3 + \phi^2, \quad p(\phi) = \phi^2(3 - 2\phi), \quad \frac{W_i\beta_i(T)}{6} = L_i \frac{T - T_i}{T_i}.
\]

Here $W_i$ is a constant, $L_i$ is the latent heat per unit volume, $T_i$ is the melting point of material $i = A,B$.

To investigate steady-state interface motion, the boundary conditions will be taken in the form

\[
c|_{x \to \infty} = c_\infty, \quad \phi|_{x \to \infty} = 0, \quad \frac{\partial c}{\partial x}|_{x \to -\infty} = 0, \quad \phi|_{x \to -\infty} = 1,
\]

and the moving frame $z$ will be adopted according to the equation

\[
z = x - Vt,
\]

so that the interface (given by $\phi = 1/2$) corresponds to $z = 0$ at this frame. In the moving frame, equations \[1\] may be written by using \[2\] as

\[
\epsilon^2 \frac{\partial^2 \phi}{\partial z^2} + \frac{V}{M_1} \frac{\partial \phi}{\partial z} - \left[ \frac{\partial f_A}{\partial \phi} + c \left( \frac{\partial f_B}{\partial \phi} - \frac{\partial f_A}{\partial \phi} \right) \right] = 0,
\]

where $V$ is the velocity of the moving frame.
\[
\frac{M_2RT}{v_m} \frac{\partial^2 c}{\partial z^2} + V \frac{\partial c}{\partial z} + M_2 \frac{\partial}{\partial z} \left[ c(1 - c) \left( \frac{\partial f_B}{\partial \phi} - \frac{\partial f_A}{\partial \phi} \right) \frac{\partial \phi}{\partial z} \right] = 0. \quad (8)
\]

For further analysis we introduce the notation for the diffusion coefficient

\[ D = \frac{M_2RT}{v_m} \]

and integrate equation (8) with respect to \( z \) over an interval \([z, \infty)\). Employing the boundary conditions (5) gives

\[
D \frac{\partial c}{\partial z} + V \left( c - c_\infty \right) + M_2 c (1 - c) \left( \frac{\partial f_B}{\partial \phi} - \frac{\partial f_A}{\partial \phi} \right) \frac{\partial \phi}{\partial z} = 0. \quad (9)
\]

3 An Approximation of a Small Impurity Concentration

Let us examine a dilute binary alloy with initial impurity concentration \( c_\infty \ll 1 \). For this purpose we shall consider the expansion in terms \( c_\infty \) for the phase-field, the solute concentration, and the temperature

\[
\phi(z) = \phi_0(z) + c_\infty \phi_1(z) + O(c_\infty^2), \quad (10)
\]
\[
c(z) = c_\infty c_1(z) + O(c_\infty^2), \quad (11)
\]
\[
T = T_0 + c_\infty T_1 + O(c_\infty^2), \quad (12)
\]

As a result, in the zeroth-order approximation, from (7) by using (3) we obtain the equation for \( \phi_0(z) \)

\[
\epsilon^2 \frac{\partial^2 \phi_0}{\partial z^2} + \frac{V}{M_1} \frac{\partial \phi_0}{\partial z} - \left( \frac{W_A}{4} \frac{\partial g}{\partial \phi} \bigg|_{\phi_0} + \frac{W_A \beta A}{6} \frac{\partial p}{\partial \phi} \bigg|_{\phi_0} \right) = 0, \quad (13)
\]

The solution of (13), which satisfies the boundary conditions (5), describes the phase field during the solidification of a pure material \( A \) and has the form

\[
\phi_0(z) = \frac{1}{2} \left[ 1 - \tanh \left( \frac{z}{2l_A} \right) \right], \quad (14)
\]

where \( l_A \) is the interface thickness and the interface velocity \( V \) is related to the temperature \( T_0 \) by the relationship

\[
V = -M_1 l_A W_A \beta A(T_0) = \frac{6M_1 l_A L_A}{T_A} (T_A - T_0), \quad (15)
\]

which determines the interface kinetics for a pure material. The relationship (15) corresponds to the model of collision limited growth [7] with a kinetic coefficient

\[
\mu = \frac{6M_1 l_A L_A}{T_A}, \quad T_0 = T_A - \frac{V}{\mu}. \quad (16)
\]
\[ e^2 \partial^2 \phi_1 \partial z^2 \frac{V}{M_1} \frac{\partial \phi_1}{\partial z} - \left[ \phi_1 \frac{\partial^2 f_A}{\partial \phi^2} \left|_{\phi_0, T_0} \right. + T_1 \frac{\partial^2 f_A}{\partial T \partial \phi} \left|_{\phi_0, T_0} \right. \\
+ c_1 \left( \frac{\partial f_B}{\partial \phi} - \frac{\partial f_A}{\partial \phi} \right) \right]_{\phi_0, T_0} = 0, \quad (17) \]

\[ \frac{\partial c_1}{\partial z} + \frac{V}{D} (c_1 - 1) + c_1 \frac{\partial \Delta F}{\partial z} = 0, \quad (18) \]

where function \( \Delta F(z) \) is defined by expression

\[ \Delta F(z) = \frac{v_m}{RT_0} \left[ f_B(\phi_0(z), T_0) - f_A(\phi_0(z), T_0) \right], \quad (19) \]

Taking into account the boundary conditions (5), the solution of (18) is

\[ c_1(z) = \frac{V}{D} \int_{-\infty}^{z} e^{\frac{V(z'-z)}{D} + \Delta F(z') - \Delta F(z')} dz' \quad (20) \]

The point \( z = 0 \) corresponds to the solid-liquid interface, i.e. \( \phi(0) = \phi_0(0) = \frac{1}{2} \), and to the inflection of the phase-field, therefore

\[ \phi_1|_{z=0} = 0, \quad \frac{\partial^2 \phi_1}{\partial z^2} \bigg|_{z=0} = 0. \quad (21) \]

As for metallic systems \( M_1 \sim 10^8 \text{cm}^3/\text{J} \cdot \text{s} \), then the relation \( V/M_1 \ll 1 \) will be satisfied. Taking into account the conditions (21) at \( z = 0 \), one can find from (17) the relationship between \( T_1 \) and \( c_1 \)

\[ T_1 = -\left( \frac{\partial f_B}{\partial \phi} - \frac{\partial f_A}{\partial \phi} \right) \bigg|_{\phi_0, T_0} c_1|_{z=0}. \quad (22) \]

Equations (11), (12), (16), and (22) give the expression for the temperature

\[ T = T_A - \frac{V}{\mu} - m(V)c|_{z=0}, \quad (23) \]

where the function \( m(V) \) is defined by

\[ m(V) = \left. \frac{\partial f_B}{\partial \phi} - \frac{\partial f_A}{\partial \phi} \right|_{\phi_0, T_0} = \frac{W_B \beta_B(T) - W_A \beta_A(T)}{W_A \frac{\partial \beta_A}{\partial T}} \bigg|_{T=T_A-V/\mu} \quad (24) \]
4 Stationary Interface

Now we consider the solute field due to the stationary solid-liquid interface, at \( V = 0 \), which corresponds to the equilibrium state. Let us introduce the definitions for the bulk concentrations in the liquid \( c_L = c(z \to \infty) \) and in the solid \( c_S = c(z \to -\infty) \). For a stationary interface, first it follows from (16) that \( T_0 = T_A \), and second the equation (18) gives the solute field

\[
\frac{c(z)}{c_L} = e^{-\Delta F(z)},
\]

which leads to the equilibrium partition coefficient

\[
k_e = \frac{c_S}{c_L} = \exp[-\Delta F(z \to -\infty)] = \exp\left(-\frac{v_m L_B (T_A - T_B)}{RT_A T_B}\right).
\]

This expression has the same form as in [6], where the equilibrium partition coefficient has been obtained from a simplified set of equations in which the effects of interface attachment kinetics are eliminated.

Using (4), from equation (24) at \( T_0 = T_A \) we obtain

\[
m_0 = m(0) = \frac{L_B T_A}{L_A T_B} (T_A - T_B).
\]

The solute concentration at the interface \( z = 0 \), in accordance with (25), is

\[
c|_{z=0} = c_L \exp\left(-\frac{v_m}{RT_A} \left[W_B - W_A + 1 \frac{L_B (T_A - T_B)}{T_B}\right]\right).
\]

Thus equations (23), (27), and (28) give the temperature at the equilibrium solid-liquid interface

\[
T = T_A - m_0 c|_{z=0} = T_A - m_0 \exp\left(-\frac{v_m}{RT_A} \left[W_B - W_A + 1 \frac{L_B (T_A - T_B)}{T_B}\right]\right) c_L = T_A - m_e c_L,
\]

which yields the following equation for equilibrium liquidus slope

\[
m_e = \frac{L_B T_A}{L_A T_B} (T_A - T_B) \exp\left(-\frac{v_m}{RT_A} \left[W_B - W_A + \frac{L_B (T_A - T_B)}{2T_B}\right]\right).
\]

5 Large-Velocity Asymptotics

To investigate the behavior of the solute concentration under rapid solidification conditions, we consider an asymptotic analysis in the limit \( V \gg 1 \). The
solution (20) can be written in the form
\[ c_1(z) = \frac{V}{D} \int_0^\infty e^{-V z'/D + \Delta F(z-z') - \Delta F(z)} dz'. \] (31)

Applying the Laplace’s theorem about asymptotic expansions to this integral, we obtain the solute field with an accuracy to second order
\[ c_1(z) = \frac{c(z)}{c_\infty} = 1 - \frac{D}{V} \frac{\partial \Delta F}{\partial z}. \] (32)

According to (32), a maximum value of solute is reached at \( z = 0 \). Therefore the segregation coefficient at large velocities is given by
\[ k = \frac{c_\infty}{c|_{z=0}} = \left. \frac{1}{1 - \frac{D}{V} \frac{\partial \Delta F}{\partial z}} \right|_{z=0} = 1 + \frac{D}{V} \left. \frac{\partial \Delta F}{\partial z} \right|_{z=0} = 1 - \frac{D}{V} \frac{v_m}{4l_A VRT} \left. \left( \frac{\partial f_B}{\partial \phi} - \frac{\partial f_A}{\partial \phi} \right) \right|_{\phi = 1/2}. \] (33)

For the sharp-interface model the nonequilibrium segregation coefficient has been derived by Aziz [9] in the limit of dilute alloy is
\[ k^{(a)} = \frac{k_e + V/V_D}{1 + V/V_D}, \] (34)

where diffusive speed \( V_D \) is a characteristic trapping velocity. For \( V/V_D \gg 1 \) the segregation coefficient \( k^{(a)} \) can be approximated by
\[ k^{(a)} = 1 - (1 - k_e) \frac{V_D}{V}. \] (35)

A comparison of the equations (33) and (35) gives
\[ V_D = \frac{D}{4l_A (1 - k_e)} \frac{v_m}{RT} \left. \left( \frac{\partial f_B}{\partial \phi} - \frac{\partial f_A}{\partial \phi} \right) \right|_{\phi = 1/2, T_0} \] (36)

According to (36), the diffusive speed \( V_D \) depends on the diffusion coefficient, on the temperature, and on the difference of free energy densities of the pure materials.

6 Numerical Calculations

To validate the obtained solution, we will compare it with numerical solutions of the steady-state governing equations (7) and (8). The material parameters used in the numerical calculations are given in Table 1. These parameters are similar to parameters employed in [6] and correspond to the alloy Ni–Cu [2].
Table 1. Thermophysical properties used in calculations

| Parameter | Value      | Reference |
|-----------|------------|-----------|
| \(L_A\)  | 2350 J/cm² | [6]       |
| \(L_B\)  | 1725 J/cm² | [6]       |
| \(T_A\)  | 1728 K     | [6]       |
| \(T_B\)  | 1358 K     | [6]       |
| \(D\)    | \(10^{-5}\) cm²/ | [6]       |
| \(\sigma\) | \(2.8 \times 10^{-5}\) J/cm² | [6] |
| \(l_A\)  | 6.48 \times 10^{-8}\) cm | [6] |
| \(v_m\)  | 7.4 cm³/mol | [2]       |
| \(\mu\)  | 24 cm/(s·K) | [10]      |

The value of kinetic coefficient was set to \(\mu = 24\) cm/(s·K) according to the work [10] in which good agreements between the model for dendritic growth and experimental data have been achieved. The far-field concentration was set to \(c_\infty = 0.1\). The parameter \(\epsilon\) is related to the surface energy \(\sigma\) and to the interface thickness \(l_A\) by equation \(\epsilon^2 = 6\sigma l_A\) [2,6]. The parameters \(W_A\) and \(W_B\) were chosen to be equal and are given as \(W_A = W_B = W = 12\sigma/l_A\) [6].

Employing (3) and (4), a finite-difference approximation of the equations (7) and (8) on a uniform grid gives the following set of equations

\[
\frac{\phi_{i+1}^{k+1} - \phi_i^k}{\Delta t} = \frac{V}{M_1 \epsilon} \frac{\phi_{i+1}^{k} - \phi_i^{k-1}}{2\Delta x} + \frac{\phi_{i+1}^{k} - 2\phi_i^{k} + \phi_{i-1}^{k}}{\Delta x^2} - \frac{W}{4} \left( \frac{\partial q}{\partial \phi} \right)_i^k - \frac{W}{6} (c\beta_B + (1 - c)\beta_A) \left( \frac{\partial \rho}{\partial \phi} \right)_i^k, \tag{37}
\]

\[
\frac{c_{i+1}^{k+1} - c_i^k}{\Delta t} = \frac{V}{M_1 \epsilon} \frac{c_{i+1}^{k} - c_{i-1}^k}{2\Delta x} + \frac{D}{M_1 \epsilon^2} \frac{c_{i+1}^{k} - 2c_i^{k} + c_{i-1}^k}{\Delta x^2} + \frac{M_2}{M_1 \epsilon^2} \frac{q_{i+1}^{k} - q_{i-1}^k}{2\Delta x}, \tag{38}
\]

\[
q_i^k = c_i^k (1 - c_i^k) \left[ \left( \frac{\partial f_B}{\partial \phi} \right)_i^k - \left( \frac{\partial f_A}{\partial \phi} \right)_i^k \right] \frac{\phi_{i+1}^{k} - \phi_{i-1}^{k}}{2\Delta x}. \tag{39}
\]

which determine the discrete functions of the solute and of the phase field at a point \(z = i\Delta x\) on a \((k+1)\)th step of iteration with a time step \(\Delta t\). To equalize the velocity \(V\) of the moving frame with the velocity of the interface, we introduce the equation

\[
\tau_f \frac{dV(\tau)}{d\tau} = V(\tau) = M_1 \epsilon \frac{dz_f}{d\tau}, \tag{40}
\]
where $V_s(\tau)$ is the shift velocity of the interface relative to the moving frame, $\tau_f$ is an accessory parameter, $\tau$ is a time variable corresponding to the iteration process, and the interface coordinate $z_f$ is given by the condition $\phi(z_f) = 1/2$. A finite-difference approximation of equation (40) gives

$$\frac{V^{k+1} - V^k}{\Delta t} = \frac{cM_1 z_f^{k+1} - z_f^k}{\tau_f}.$$  \hspace{1cm} (41)

Results of numerical calculations of the equations (37)–(41) are shown in the following figures. Fig. 1 shows a good agreement between the analytical solution [equations (11), (20), (23), and (24)] and the numerical results in the wide range of undercoolings.

Fig. 1. Kinetic curve “interface velocity $V$ — initial undercooling $\Delta T$”. The solid curve shows the approximated solution, data points denote the result of the numerical calculations.

Fig. 2 shows the solute and the phase fields. At the interface, the solute field is smooth as against sharp-interface models, which gives a jump in concentration. At low undercoolings, the analytical solution gives some excessive value of solute concentration in the vicinities of the interface. The series of numerical calculations given in Fig. 2 demonstrate the degeneration of the solute to uniform field with increasing interface velocity and undercooling.
Such behavior of the solute field is in accordance with the equation (32), in which the deviation from the far-field concentration is proportional to $1/V$.

![Graph](image)

Fig. 2. Solute profiles and the phase field for different values of the initial undercooling. The solid curve shows the approximated solution, data points denote the result of numerical calculations.

7 Conclusions

Planar solidification from undercooled melt was investigated by numerical and analytical methods in the limit of small impurity concentration. Comparing the obtained results with those of [6], we note that while equilibrium partition coefficient (26) has the same form as in work [6], the expression
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The liquidus slope differs from the one given in the work \([6]\). However, the evaluated equilibrium liquidus slope has very close values, \(m_e = 306.2\) K from equation (30) and \(m_e = 306.9\) K from equation (A13) in \([6]\). The diffusive speed has a weak dependence on the temperature, Eq. (36), and can be accepted to be constant as well as the diffusive speed obtained in \([6]\). The numerical calculations presented here show a good agreement with the analytical solution that indicate a sufficient accuracy of the expansion (10)–(12).

The obtained solutions simultaneously are valid for the bulk phases and the interface. Therefore they can be suitable for the purpose of numerical simulations: for instance to construct initial splitting of adaptive finite-element grid and as a first approximation for the numerical solution of transcendental equations.

References

1. Kurz W., Fisher D.J.: Fundamentals of Solidification, 3rd ed. Aedermannsdorf: Trans Tech Publication, 1992. 305 p.
2. Wheeler A. A., Boettinger W. J., McFadden G. B.: Phase-field model for isothermal phase transitions in binary alloys. Phys. Rev. A 45 (1992) 7424–7438.
3. BiZ., Sekerka R. F.: Phase-field model of solidification of a binary alloy. Physica A 261 (1998) 95–106.
4. Wheeler A. A., Boettinger W. J., McFadden G. B.: Phase-field model of solute trapping during solidification. Phys. Rev. E 47 (1993) 1893–1909.
5. Elder K. R., Grant M., Provatas N., Kosterlitz J. M.: Sharp interface limits of phase-field models. Phys. Rev. E 64 (2001) 021604.
6. Ahmad N. A., Wheeler A. A., Boettinger W. J., McFadden G. B.: Solute trapping and solute drag in a phase-field model of rapid solidification. Phys. Rev. E 58 (1998) 3436–3450.
7. Turnbull D.: Metastable structures in metallurgy. Metall. Trans. A. 12 (1981) 695–708.
8. Olver F. W. J.: Asymptotics and Special Functions. New York: Academic Press, 1974. 584 p.
9. Aziz M. J.: Model for solute redistribution during rapid solidification. J. Appl. Phys. 53 (1982) 1158–1168.
10. Gelenko P. K., Danilov D. A.: Model for free dendritic alloy growth under interfacial and bulk phase nonequilibrium conditions. J. Crystal Growth 197 (1999) 992–1002.