The concentration intrinsic instability for crystal growth in diffusion process

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Abstract

The coupling of mass diffusion in a solution (or a melt) and the kinetic process on the solidification interface is described by a linear diffusion equation with the appropriate linear boundary conditions (J. Crystal Growth 8 (1971) 79). In the present paper, the instability and the wave-like solution of the linear problem are discussed after obtaining a full analytical solution to the governing equations and conditions. The solution is obtained by superposing a non-steady-state solution on a steady-state solution, as given in (J. Crystal Growth 8 (1971) 79). Results from the completely solved linear problem presented in this paper are different from those obtained by using only the conditions on the interface (Phys. Rev. E 60 (1999) 1901).
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1. Introduction

As suggested by many geologists, the non-linear models can be used to explain the oscillatory zoning effect observed in naturally grown crystal [1,2]. The structure variations such as the zoning, banding and striation effects have also been well observed under different laboratory conditions [3–11]. This is the case even for the process of protein crystal growth [12]. It is widely known that the structure variations are related to a non-steady-state process, which is excited by the coupling of the transport process in the bulk fluid medium with the kinetics on the solidification interface. In most cases, the interfacial kinetics is a non-linear process, which makes the coupling process also non-linear.

Based on a linear solution of the steady coupling process presented in Ref. [14], an intrinsic instability model was recently proposed to try to explain the unsteady coupling process discussed above [13]. In the model, the non-steady-state solutions were obtained by using only the linear boundary conditions without considering the transport process in the bulk fluid. In the present paper, the same physical model is re-examined,

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and the complete problem with full analytical solutions is discussed.

2. Mathematical description of the linear problem

A two-dimensional model in a Cartesian coordinate system, with the interface at $y = 0$, is presented here. The equations and conditions governing the concentration in the bulk fluid $C(x, y, t)$ and the adsorption concentration on the interface $n(x, t)$ can be written as follows [13,14]:

$$\frac{\partial C}{\partial t} = D\left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2}\right), \quad y > 0, \tag{2.1}$$

$$D\frac{\partial C}{\partial y} = \frac{D}{\Lambda}C - \frac{n}{\tau}, \quad y = 0, \tag{2.2}$$

$$-D\frac{\partial C}{\partial y} = D_s\frac{\partial^2 n}{\partial x^2} - \frac{\partial n}{\partial t}, \quad y = 0, \tag{2.3}$$

$$C = C_m(x, t), \quad y = \delta, \tag{2.4}$$

$$C = C_i(x, y), \quad t = 0. \tag{2.5}$$

Here, $C_m(x, 0) = C_i(x, \delta)$, D and D_s are respectively the bulk diffusion coefficient and the surface diffusion coefficient, D/Λ is the drift velocity of the fluid molecules entering the absorbed layer from the adjacent volume, and τ stands for the mean lifetime of an adsorbed molecule on the interface. All coefficients D, D_s, Λ and τ are assumed as constants. Eqs. (2.2) and (2.3) describe the kinetics process on the interface [14], whereas Eq. (2.1), together with boundary conditions (2.4) and (2.5), represent the diffusion process. Relationship (2.4) is the upper boundary condition of the diffusion region, where δ may be considered either as the thickness of the diffusion boundary layer [14] or a distance far from the interface [2]. Relationship (2.5) is the initial condition, which may be omitted in certain cases, such as the developed process. The boundary conditions at $x = \pm L$ should be available if a finite interface region $|x| \leqslant L$ is considered. In this case, $2L$ stands for the typical scale of the step width or the scale of solidification interface, which may be considered as infinite in some cases.

Diffusion equation (2.1) describes the transport process in the fluid region where $y > 0$, and can be solved with the boundary conditions of a closed region, e.g. a region that is rounded within $x = \pm L$, $y = 0$ and $y = \delta$. Considering all these, we should not neglect boundary condition (2.4) when trying to completely define the problem of the coupling process. Furthermore, the transport process should be coupled with the interfacial kinetics, described by the conditions at boundary $y = 0$ in Eqs. (2.2) and (2.3). Thus, the physical problem should be solved from the equation under a complete set of boundary conditions, which should include both the coupling conditions at $y = 0$ and the diffusion boundary condition at $y = \delta$.

Both Eq. (2.1) and conditions (2.2)–(2.5) are linear in this model, and the coupling problem of the bulk concentration field $C(x, y, t)$ and interfacial concentration field $n(x, t)$ can be de-coupled. By using condition (2.2), condition (2.3) can be reduced to a condition of bulk concentration $C(x, y, t)$ as

$$-\frac{\partial C}{\partial y} = \tau\left(\frac{1}{\Lambda} - \frac{\partial}{\partial y}\right)\left(D_s\frac{\partial^2 C}{\partial x^2} - \frac{\partial C}{\partial t}\right), \quad y = 0. \tag{2.6}$$

Diffusion equation of bulk concentration (2.1) can be solved under the boundary conditions of bulk concentration (2.6), (2.4) and initial condition (2.5). With this solution, the interfacial concentration can be obtained by condition (2.2).

3. "Perturbation" expansion

The perturbation theory is generally used to investigate the linear instability of a non-linear problem. All the solutions of a linear problem can be superposed, and there is no limitation on each of the solution to be a perturbed one. As a result, the solution of the linear problem presented in this paper may be formed by superpose a non-steady-state solution on a steady-state solution shown as follows

$$C(x, y, t) = C_0(x, y) + C_1(x, y, t). \tag{3.1}$$

The non-steady-state concentration C_1 could be either a perturbed solution when $|C_1|$ is smaller than $|C_0|$ by at least an orders of magnitude, or an

ordinary solution when $|C_1|$ is comparable or even larger than $|C_0|$.

Substituting (3.1) into the equation and conditions list in Section 2, the steady-state solution reduces into the linear steady-state problem as

$$\frac{\partial^2 C_0}{\partial x^2} + \frac{\partial^2 C_0}{\partial x^2} = 0, \tag{3.2}$$

$$C_0 = C_m, \quad y = \delta, \tag{3.3}$$

$$-\frac{\partial C_0}{\partial y} = \tau D_s \left(\frac{1}{\Lambda} - \frac{\partial}{\partial y} \right) \frac{\partial^2 C_0}{\partial x^2}, \quad y = 0. \tag{3.4}$$

The function $C_m(x, t)$ is considered as a constant as usual and a solution of steady-state linear problem (3.2)–(3.4) was presented in Ref. [14]. For the non-steady-state concentration, the linear problem is described as

$$\frac{\partial C_1}{\partial t} = D \left(\frac{\partial^2 C_1}{\partial x^2} + \frac{\partial^2 C_1}{\partial y^2} \right), \tag{3.5}$$

$$-\frac{\partial C_1}{\partial y} = \tau \left(\frac{1}{\Lambda} - \frac{\partial}{\partial y} \right) \left(D_s \frac{\partial^2 C_1}{\partial x^2} - \frac{\partial C_1}{\partial t} \right),$$
$$y = 0, \tag{3.6}$$

$$C_1 = 0, \quad y = \delta, \tag{3.7}$$

$$C_1 = C_i(x, y) - C_0(x, y), \quad t = 0. \tag{3.8}$$

In Eq. (3.7), the bulk concentration is zero at the boundary $y = \delta$. This comes from the assumption that the final solution is the superposition of a steady-state solution and a non-steady-state solution as shown in Eq. (3.1). Linear equations (3.2)–(3.4) implies that the non-steady-state solution $C_1(x, y, t)$ is independent of the steady-state solution from Eqs. (3.5)–(3.8) when initial condition (3.8) is not considered. It is noted that, boundary condition (3.7) is suitable only for a fixed boundary $y = \delta$ such as a solid boundary or to infinite. However, boundary will be changed for a free surface as $y = \delta + \delta_1$, where δ_1 is smaller than δ in order of magnitude, and boundary condition of a perturbation problem is given into

$$C_1(x, \delta + \delta_1) = C_1(x, \delta) + \delta_1 \partial C_0(x, \delta)/\partial y \tag{3.9}$$

for the free surface problem to replace boundary condition (3.7) for a solid boundary problem.

Instead of the perturbation problem, we consider a problem of only a non-steady-state, where $C_0(x, y) = 0$. In this case, boundary conditions (3.7) and (3.8) can be replaced by condition (2.4) and condition (2.5), respectively. The transformation may be introduced as follows

$$C(x, y, t) = C_1(x, y, t) - C_m,$$
$$n(x, t) = n_1(x, t) - D\tau C_m/\Lambda. \tag{3.10}$$

The concentrations C_1 satisfy Eq. (3.5) and boundary conditions (3.6)–(3.8) if C_m is a constant as usual, and the similar conclusion may be obtained.

4. Non-steady-state solution of the complete problem

Usually, the structure variations such as the striation and oscillatory zoning are related to the non-steady-state variation of the fields in the bulk fluid medium during the crystal growth, and the onset of non-steady-state variation of the field depends on the process parameters. This has generated great interests in the physics world.

If the perturbation theory is used to analyze the present problem, the steady-state solution and the non-steady-state solution can be mapped to the basic state and the perturbed state. In this case, the initial perturbation should be zero, and the initial condition (3.8) reduces to

$$C_1(x, y, 0) = 0.$$

With this assumption, the non-steady-state linear problem described by Eqs. (3.5)–(3.8) gives a zero solution to the bulk concentration $C_1(x, y, t) = 0$ and the interfacial concentration $n_1(x, t) = 0$ for the perturbation problem. Here, there exists only a basic state of steady-state solution as discussed in Ref. [14]. In this case, there is a unique steady-solution to the linear problem of the diffusion process that is described by a parabolic partial differential equation with linear boundary conditions.

To study the case of the non-steady-state problem in Eqs. (3.5)–(3.8), the developed process will be considered where initial condition (3.8) can be omitted. Similar to Ref. [13], the non-steady-state

solution can be written as

$$C_1(x, y, t) = c(y) \exp(\omega t + ikx). \tag{4.1}$$

Here, k is a real number and ω may be a complex number. Substituting (4.1) into (3.5)–(3.7), we can have a linear problem of function $c(y)$ as

$$\frac{d^2 c}{dy^2} = \left(\frac{\omega}{D} + k^2\right)c, \tag{4.2}$$

$$\frac{dc(0)}{dy} = \frac{\tau}{\Lambda} \frac{D_s k^2 + \omega}{\tau(D_s k^2 + \omega) + 1} c(0), \tag{4.3}$$

$$c(\delta) = 0. \tag{4.4}$$

The general solution of Eq. (4.2) is

$$c(y) = a_1 \exp\left(\sqrt{\frac{\omega}{D} + k^2}\, y\right)$$
$$+ a_2 \exp\left(-\sqrt{\frac{\omega}{D} + k^2}\, y\right), \tag{4.5}$$

where a_1 and a_2 are constants to be determined by boundary condition (4.3) and (4.5). By using condition (4.4), solution (4.5) becomes

$$c(y) = a_3 \, \text{sh}\left[\sqrt{\frac{\omega}{D} + k^2}(y - \delta)\right] \tag{4.6}$$

with ω being a complex number in constant a_3

$$a_3 = -2a_2 \exp\left(-\sqrt{\frac{\omega}{D} + k^2}\delta\right). \tag{4.7}$$

However, the non-steady-state solution can have a constant multiply factor because that the equation and boundary conditions are linear and uniform.

By using solution (4.6), we can get, from relationship (4.1) and (4.2), the bulk concentration field and the interfacial concentration field as shown here

$$C_1(x, y, t) = a_3 \, \text{sh}\left[\sqrt{\frac{\omega}{D} + k^2}(y - \delta)\right] e^{\omega t + ikx}, \tag{4.8}$$

$$n_1(x, t) = -a_3 \tau D\left[\frac{1}{\Lambda} \text{sh}\left(\sqrt{\frac{\omega}{D} + k^2}\delta\right)\right.$$
$$\left. + \sqrt{\frac{\omega}{D} + k^2}\, \text{ch}\left(\sqrt{\frac{\omega}{D} + k^2}\delta\right)\right] e^{\omega t + ikx}. \tag{4.9}$$

The non-steady-state problem can be completely solved once the relationship between ω and k is given. Consequently, full analytical solutions for both the bulk concentration $C(x, y, t) = C_0(x, y) + C_1(x, y, t)$ and the interfacial concentration $n(x, t) = n_0(x, y) + n_1(x, y, t)$ are achieved for the linear problem.

Similar approach can be applied to the problem with a free surface, and boundary condition (3.7) will be replaced by (3.9). In this case, the perturbed boundary δ_1 is written as

$$\delta_1 = \delta * \exp(\omega t + ikx), \tag{4.10}$$

where $\delta*$ is a constant to be determined. Submitting (4.1) and (4.10) into the equation and boundary conditions, the problem can then be solved.

5. Dispersion relation

Substituting solution (4.6) into boundary condition (4.3), the dispersion condition can be written as follows

$$\sqrt{\frac{\omega}{D} + k^2} = -\frac{\tau}{\Lambda} \frac{D_s k^2 + \omega}{\tau(D_s k^2 + \omega) + 1}$$
$$\times \text{th}\left(\sqrt{\frac{\omega}{D} + k^2}\delta\right). \tag{5.1}$$

To simplify the analysis, the case of infinite extension in the y direction is discussed in detail. Translating into mathematical term, this means that δ is set to approach infinite. Under this condition, term $\text{th}[(k^2 + \omega/D)^{1/2}\delta] \to 1$, and dispersion relation (5.1) may be reduced to a third-order algebraic equation of ω shown here,

$$\omega^3 + f_2\omega^2 + f_1\omega + f_0 = 0. \tag{5.2}$$

Coefficient f_2, f_1 and f_0 are real numbers and can be expressed as

$$f_2 = k^2(D + 2D_s) - \left(\frac{D}{\Lambda^2} - \frac{2}{\tau}\right),$$

$$f_1 = k^4 D_s(2D + D_s)$$
$$- 2k^2\left(-\frac{D + D_s}{\tau} + \frac{DD_s}{\Lambda^2}\right) + \frac{1}{\tau^2},$$

$$f_0 = k^6 DD_s^2 - k^4 DD_s\left(-\frac{2}{\tau} + \frac{D_s}{\Lambda^2}\right) + k^2\frac{D}{\tau^2}. \tag{5.3}$$

The dispersion relation is given by the solution of Eq. (5.2), and can be analytically written as

$$\omega_1 = \alpha + \beta + f_2/3,$$
$$\omega_2 = \alpha\varepsilon + \beta\varepsilon^2 + f_2/3,$$
$$\omega_3 = \alpha\varepsilon^2 + \beta\varepsilon + f_2/3. \tag{5.4}$$

Here, ε is the cubic root of 1 and is given as

$$\varepsilon = -\frac{1}{2} + i\frac{\sqrt{3}}{2}, \quad \varepsilon^2 = -\frac{1}{2} - i\frac{\sqrt{3}}{2}, \quad \varepsilon^3 = 1. \tag{5.5}$$

The fundamental solutions of α and β are

$$\alpha = \left(-\frac{q}{2} + \sqrt{\frac{q^2}{4} + \frac{p^3}{27}} \right)^{1/3},$$

$$\beta = \left(-\frac{q}{2} - \sqrt{\frac{q^2}{4} + \frac{p^3}{27}} \right)^{1/3} \tag{5.6}$$

with p and q are defined as

$$p = f_1 - \frac{1}{3}f_2^2, \quad q = f_0 - \frac{1}{3}f_1 f_2 + \frac{2}{27}f_2^3. \tag{5.7}$$

The criterion forum of Eq. (5.2) is

$$\Delta = -4p^3 - 27q^2. \tag{5.8}$$

The three roots ω_1, ω_2 and ω_3 are all real numbers if $\Delta \geq 0$. If $\Delta < 0$, we get one real number and two conjugate complex numbers for solutions.

The oscillatory zoning is related to the wave solution of the concentration fields, which requires a solution of complex ω under the condition of $\Delta < 0$. It requires

$$\left(\frac{2}{27}f_2^3 - \frac{1}{3}f_1 f_2 + f_0 \right)^2 > \frac{4}{27}\left(\frac{1}{3}f_2^2 - f_1 \right)^3. \tag{5.9}$$

By using definition (5.3), we can conclude that the right-hand side of (5.9) is usually positive, specially for the case of larger wave number $(k\Lambda)^2 \gg 1$:

$$\frac{f_2^2}{3} - f_1 = \frac{1}{6}\left[k^2(D - D_s) - \frac{D}{\Lambda} \right]^2$$
$$+ \frac{1}{6}\left[k^2(D - D_s) - \frac{1}{\tau} \right]^2$$
$$+ \frac{1}{3}\left(\frac{1}{2\tau^2} - \frac{4D}{\tau\Lambda^2} \right) > 0. \tag{5.10}$$

In general, the bulk diffusion coefficient D is three orders of magnitude larger than the interfacial diffusion coefficient D_s, making terms associated with D_s in formula (5.3) negligible.

Obviously, requirement (5.9) is not easily explainable under general condition. A special case was examined in Ref. [13] where the parameters were given as

$$D = 5.5 \times 10^{-6} \text{ cm}^2/\text{s}, \quad D_s = 1.0 \times 10^{-9} \text{ cm}^2/\text{s},$$
$$t = 0.25 \text{ s}, \quad \Lambda = 1.0 \times 10^{-3} \text{ cm}.$$

In the long wavelength approximation $(k\Lambda)^2 \ll 1$, requirement (5.9) can be reduced to

$$(k\Lambda)^2 < 0. \tag{5.11}$$

In the short wavelength approximation $(k\Lambda)^2 \gg 1$, requirement (5.9) can be reduced to

$$(k\Lambda)^2 > 0. \tag{5.12}$$

Results of (5.11) and (5.12) indicate no wave-like solution of $\exp[i(kx - \omega_i t)]$ in the case of long wavelength approximation. However, there may have a wave-like solution in short wavelength approximation.

Based on the theory of linear parabolic differential equation with linear boundary conditions, the wave-like solution may exist for the linear problem of infinite extension, but does not exist for the linear problem of finite extension [15], which is the case related to the crystal growth.

6. Discussions

Coupling of the diffusion process in the fluid medium with the kinetic process on the interface is studied in the present paper. A complete analytical solution to this coupling process can be reached by solving a parabolic differential equation of linear diffusion process with linear boundary conditions, which model the process. Limiting the problem to a half-infinite space, the solution may be expressed as the superposition of a steady-state solution and a non-steady-state solution of the developed process, where there exists a wave-like solution with short wave length approximation. Features in the complete solution to the problem discussed in the present paper are different from those given by using only the conditions on the interface. However, it is still not physically clear how to relate the initial deviation from the steady-state process

to the developed state of the non-steady-state process.

Based on the conclusion in the present paper, the wave-like solution of a non-steady-state process may exist under certain conditions, such as the infinite extension in the x direction with the short wavelength approximation. The so-called intrinsic instability was described by a linear model, which gave a wave-like solution and the dispersion relation only from the boundary conditions at the interface but not coupled with the diffusion process in the liquid medium [13]. Therefore, the model [13] may be considered as an incomplete problem, and its conclusion is not quite clear in physics and needs to be studied further in the future.

It should be pointed out that by analyzing the linear problem, it is not easy to get the wave-like solution to the coupling process of diffusion in a solution (or a melt) with the kinetics on the interface for the general cases. Thus, certain non-linear factors should be introduced when trying to explain the oscillatory zoning effect [1,2]. The solution of the non-steady-state process described by Eqs (3.5)–(3.8) is not related to the physical concept of the instability on a steady-state process, and is independent of the solution of steady-state process in the linear problem for a developed process. It is believed that, the non-linear problem should be introduced to study the coupling process, and more factors influencing the instability of a basic state could be analyzed in greater details.

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