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Directional solidification of binary melts with a non-equilibrium mushy layer

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Abstract

When the melt or solution solidifies a constitutionally supercooled mushy layer is frequently formed ahead of the phase transition boundary. This leads to nucleation and growth mechanisms of newly born solid particles within a mush. The latter is responsible for the structures and properties appearing in the crystal. The process of solidification with a supercooled mushy layer is analytically described on the basis of two joint theories of directional and bulk crystallization. Such characteristics as the constitutional supercooling, the solid fraction and the radial density distribution function of solid particles in a mushy layer are found. The complex structure of the non-equilibrium mushy layer is completely recognized.

Keywords: Solidification; Mushy layer; Crystal growth; Constitutional supercooling

1. Introduction

Theoretical studies of the solidification processes in melts and solutions are usually based on the thermodiffusion Stefan-type models with a planar front. In the course of investigation this model needs to find the concentration of the impurity and temperature of the matter both in the liquid and the growth crystal. The analyses are complicated by the need to apply boundary conditions at solid/liquid interface which are evolving with time and whose position must be found as part of the calculation. The temperature of the phase transition (liquidus) is variable and unknown too. It is dependent on the local impurity concentration and determined from the phase diagram [1,2]. Some Stefan-type problems have been solved completely in simple geometries in classical studies (for example, solidification from a plane wall, inward and outward crystallization processes of cylinders and spheres, is considered in Refs. [3–5]). In these early studies the domain of crystallization is divided into two regions: melt (liquid phase) and crystal (solid phase) separated by the moving boundary of phase transition (solidification front). However, the solidification of binary melts is rather frequently accompanied by the appearance of supercooled regions, i.e., regions in the liquid phase, the temperature of which is lower than the equilibrium temperature of phase transition, which depends on the local impurity concentration. One of the supercooling mechanisms termed "constitutional" was revealed for the first time by Ivantsov [6]. This mechanism occurs in the following manner. When the front moves into the liquid and replaces the solute impurity ahead itself, the solute concentration increases. As a result, the phase transition temperature decreases at the front (accordingly to the phase diagram) and is an increasing function with increasing distance from the phase interface. When the liquid temperature goes below its freezing point a constitutionally supercooled region arises ahead of the front. Elements of the new phase may start spontaneous generation in supercooled zone in the form of dendrites or particles by means of bulk nucleation. In other words, this

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Nomenclature

f	radial density distribution function of solid particles
g_s and g_l	temperature gradients in the crystal and the melt
L_V	latent heat of crystallization
r	radius of crystal in the mush
V	solidification speed
z	spatial coordinate

Greek symbols

$\Delta\theta$	constitutional supercooling
φ	volume fraction of solid crystals
λ	thermal conductivity
θ	temperature
θ_p	phase transition (liquidus) temperature
σ	impurity concentration

Subscripts

's' and 'l' stand for the properties of solid and liquid phases, respectively

region (termed "two-phase" or "mushy" layer) is consisted of the mixed solid and liquid phases.

Solidification problems of binary alloys in the presence of supercooled regions have been studied by a number of investigators (see, among others, [2,7–12]). However, with a few exceptions, these works are devoted to analytical and numerical studies of a mushy layer treated as quasi-equilibrium. The latter implies that the constitutional supercooling is entirely compensated by a latent heat of crystallization, which is eliminated by growing elements of the new phase. As a result, the mushy layer temperature attains the liquidus temperature. This assumption essentially simplifies the problem under consideration. However, solutions obtained in this manner cannot describe the internal and topological structures of a mushy layer. Furthermore, strictly speaking, the constitutional supercooling ahead of the phase transition front does not disappear completely. For this reason, in order to construct the theory of solidification in the presence of a supercooled region, the theoretical model must include some kinetic factors responsible for the formation of elements of the new phase in a mushy layer. In this paper, we develop the theory of directional solidification of binary alloys with a mushy layer where the supercooling plays a predominant role.

2. Governing equations for a mush

Let us consider the steady-state crystallization process associated with the frame of reference moving with a constant speed V along axis z. A mushy layer separates purely solid and liquid phases. In this model we imagine that the mush/liquid interface, at which the temperature is equal to the local liquidus temperature, can be maintained at the fixed horizontal position $z = 0$. The solid/mush interface $z = -h$ is left as a free boundary to be determined as a part of the solution.

The temperature θ and the composition σ of the interstitial liquid are assumed to be uniform over lengthscales typical of the intercrystal spacing. Then differential equations describing conservation of heat and solute can be written as (e.g. [2,7,8,13,14])

$$\frac{\mathrm{d}}{\mathrm{d}z}\left(\lambda\frac{\mathrm{d}\theta}{\mathrm{d}z}\right) - VL_V\frac{\mathrm{d}\varphi}{\mathrm{d}z} = 0, \tag{1}$$

$$-V\frac{\mathrm{d}}{\mathrm{d}z}((1-\varphi)\sigma) = \frac{\mathrm{d}}{\mathrm{d}z}\left(D\frac{\mathrm{d}\sigma}{\mathrm{d}z}\right) + k\sigma V\frac{\mathrm{d}\varphi}{\mathrm{d}z}. \tag{2}$$

The volume fraction of solid crystals in mush is denoted by φ, k is the impurity distribution factor (k represents the ratio of the solute concentration in the solid and liquid phases at the phase transition boundary), L_V is the latent heat of solidification per unit volume. The thermal conductivity λ and the solutal diffusivity D are functions of φ: $\lambda(\varphi) = \lambda_l(1-\varphi) + \lambda_s\varphi$, $D(\varphi) = D_l(1-\varphi)$, where subscripts 's' and 'l' denote properties of the solid and liquid phases, respectively (e.g. [1,2,9,14,15]). We neglect the right hand side of Eq. (1), because the relaxation time $\tau_a = l^2/a$ of temperature fields is essentially less then the relaxation time $\tau_D = l^2/D_l$ of the diffusion field, i.e. $\tau_a/\tau_D \sim 10^{-3}$–$10^{-4}$ (l is a characteristic length scale, and a is the temperature diffusivity coefficient). The temperature fields in crystal and melt phases will be governed by constant temperature gradients g_s and g_l. The boundaries solid/mush ($z = -h$) and mush/liquid ($z = 0$) are determined from the conditions: temperatures at these boundaries are equal to the local liquidus temperatures, i.e. supercooling is equal to zero. The traditional heat and mass balance boundary conditions at $z = 0$ and $z = -h$ described in [2,3,7,13] hold true.

It was demonstrated previously that the speed of solidification can be written in the form [10,12]

$$V = \frac{\lambda_s g_s - \lambda_l g_l}{L_V}.$$

Let us especially emphasize that this speed describes not only the non-equilibrium regime under consideration but also the frontal and equilibrium mushy layer regimes studied previously.

Integrating (1) and keeping in mind that the temperature gradient is continuous and $\varphi = 0$ at the mush/liquid interface, we have

$$\lambda(\varphi)\frac{\mathrm{d}\theta}{\mathrm{d}z} - VL_{\mathrm{V}}\varphi = \lambda_{\mathrm{l}}g_{\mathrm{l}}. \tag{3}$$

Let us use the Scheil equation instead of (2) to describe the mass transfer in a mush [9]

$$\sigma = \frac{\sigma_0}{(1-\varphi)^{1-k}}, \tag{4}$$

where σ_0 stands for the concentration in the liquid. Formula (4) is frequently applied by a number of investigators (see, among others, [9,16]). It is a good approximation for the impurity redistribution during the crystal growth for a wide range of experimental conditions [17]. We use expression (4) as simplest approximation comprising the effect of impurity accumulation at the moving phase transition boundary (the key feature for constitutionally supercooled mushy layer). Mathematically, this law follows from Eq. (2) for $D = 0$.

The local phase transition temperature is determined by liquidus equation (see, for example, [1,2]) of the linear form $\theta_{\mathrm{p}}(\sigma) = \theta_{\mathrm{p}}^0 - m\sigma$, where m is the liquidus slope coefficient and θ_{p}^0 is the freezing point at $\sigma = 0$. Combining this linear law and expressions (3) and (4), we arrive at the following equation for supercooling in a mush $\Delta\theta(z) = \theta_{\mathrm{p}}(\sigma(z)) - \theta(z)$:

$$-b_1\frac{\mathrm{d}}{\mathrm{d}z}\Delta\theta = \frac{b_2+\varphi}{b_3+\varphi} + b_4\frac{1}{(1-\varphi)^{2-k}}\frac{\mathrm{d}\varphi}{\mathrm{d}z},$$
$$b_1 = \frac{\lambda_{\mathrm{s}}-\lambda_{\mathrm{l}}}{VL_{\mathrm{V}}},\quad b_2 = \frac{\lambda_{\mathrm{l}}g_{\mathrm{l}}}{VL_{\mathrm{V}}},\quad b_3 = \frac{\lambda_{\mathrm{l}}}{\lambda_{\mathrm{s}}-\lambda_{\mathrm{l}}}, \tag{5}$$
$$b_4 = (1-k)m\sigma_0\frac{\lambda_{\mathrm{s}}-\lambda_{\mathrm{l}}}{VL_{\mathrm{V}}},$$

with boundary conditions $\Delta\theta(0) = \Delta\theta(-h) = 0$. Eq. (5) depends on unknown function φ, which characterizes nucleation and growth mechanisms in a mushy layer. How to express this function in explicit form is discussed below.

3. The interior structure of a mushy layer

In order to describe a mushy layer let us apply the theory of bulk crystallization developed in [18] (see also [13]). We treat a mush as suspension of spherical solid particles submerged in a macroscopically homogeneous supercooled liquid. The nucleation rate of crystal particles written out in accordance with the Frenkel–Zeldovich theory [19,20] has the form

$$I = I_*\exp\left(-\frac{p}{\Delta\theta^2}\right), \tag{6}$$

where p is the dimensional Gibbs number and I_* is a pre-exponential factor considered to be known. Solid nuclei exceeding some critical value tend to further growth whereas smaller particles vanish [19]. The spherical particles with radius r undergo a rise in accordance with expression (e.g. [13,21])

$$\frac{\mathrm{d}r}{\mathrm{d}t} = \frac{\beta_*\Delta\theta}{1+\beta_*(L_{\mathrm{V}}/\lambda_{\mathrm{l}})r}, \tag{7}$$

where β_* stands for the kinetic coefficient. The evolution of solid particles in a mushy layer is described by a kinetic equation for density $f(t,z,r)$ as

$$\frac{\partial f}{\partial t} + \frac{\partial}{\partial r}\left(\frac{\mathrm{d}r}{\mathrm{d}t}f\right) = 0, \tag{8}$$

supplemented by the boundary condition of the form

$$\left.\frac{\mathrm{d}r}{\mathrm{d}t}f\right|_{r=0} = I_*\exp\left(-\frac{p}{\Delta\theta^2}\right). \tag{9}$$

Here the critical radius (critical value) of growing crystals is chosen as zero. Let us express function φ in the form

$$\varphi = \int_0^\infty \frac{4\pi}{3}r^3 f(t,z,r)\mathrm{d}r. \tag{10}$$

Such possible mechanisms as agglomeration and coalescence of particles as a result of their growth and interaction are not considered by the theory under consideration. The latter means that the bulk fraction φ is limited by a critical value $\varphi_{\mathrm{crit}} < 1$, which is responsible for the physically correct scope of our theory.

In the moving frame of reference equations (7)–(9) take the following form:

$$-(1+qr)\frac{\mathrm{d}r}{\mathrm{d}z} = \frac{\beta_*}{V}\Delta\theta, \tag{11}$$
$$-\frac{\partial f}{\partial z} + \frac{\beta_*}{V}\Delta\theta\frac{\partial}{\partial r}\left(\frac{f}{1+qr}\right) = 0, \tag{12}$$
$$f|_{r=0} = \frac{I_*}{\beta_*}\frac{1}{\Delta\theta}\exp\left(-\frac{p}{\Delta\theta^2}\right), \tag{13}$$

where $q = \beta_* L_{\mathrm{V}}/\lambda_{\mathrm{l}}$. Now, in equations (11)–(13) and (10), $f = f(z,r)$ is independent of t.

Eq. (12) supplemented by expressions (13) and $f|_{z=0} = 0$ gives

$$f = \left(1+\beta_*\frac{L_{\mathrm{V}}}{\lambda_{\mathrm{l}}}r\right)\eta(x(z)-y(r))H(x(z)-y(r)), \tag{14}$$

where the following designations are introduced:

$$x(z) = \frac{\beta_*}{V}\int_z^0\Delta\theta(\xi)\mathrm{d}\xi,\quad y(r) = \int_0^r\left(1+\beta_*\frac{L_{\mathrm{V}}}{\lambda_{\mathrm{l}}}r\right)\mathrm{d}r,$$
$$\eta(u) = \frac{I_*}{\beta_*}\frac{1}{\Delta\theta(u)}\exp\left(-\frac{p}{\Delta\theta(u)^2}\right),\quad H(u)\text{—Heaviside function.}$$

From the physical point of view, the Heaviside function entering in (14) designates that the size of the solid particles is limited by a maximum value, which corresponds to the size of the crystals nucleated at the liquid/mush interface (this size is determined by Eq. (25). Integrating (11) and taking into account that $r = 0$ at $z = \zeta$, we have

$$r = (\sqrt{1+2q(x(z)-x(\zeta))} - 1)/q. \tag{15}$$

Eq. (15) defines radius $r(z)$ of crystals appearing at point $z = \zeta$ within a mushy layer.

4. How to calculate the constitutional supercooling within a mush?

Expressions (14) and (15) determine unknowns entering into the solid fraction φ from (10). However, it should be noted that Eq. (10) does not express $\varphi(z)$ in explicit form because $\Delta\theta(z)$ is dependent of φ accordingly to (5). In order to solve this nonlinear problem let us adapt the method detailed in Ref. [13] for single-component supercooled liquids.

So, let us introduce new variable ζ instead of r for any constant z by means of expression $x(\zeta) = x(z) - y(r)$. It follows here from that

$$\frac{\beta_*}{V}\Delta\theta(\zeta)\mathrm{d}\zeta = (1+qr)\mathrm{d}r,$$

and limits $r = 0$ and $r = r|_{\zeta=0}$ of integration transform to corresponding limits $\zeta = z$ and $\zeta = 0$ in terms of ζ. Replacing r by ζ in (10) and taking into consideration (14) and (15), we arrive at

$$\varphi(z) = \frac{4\pi}{3}\frac{I_*}{V}\int_z^0 w(z,\zeta)\exp(pS(\zeta))\mathrm{d}\zeta, \tag{16}$$

where $w(z,\zeta) = q^{-3}(\sqrt{1+2q(x(z)-x(\zeta))}-1)^3$, $S(\zeta) = -1/\Delta\theta(\zeta)^2$.

Parameter p (expressed in $(^\circ\mathrm{C})^2$) entering in Eq. (16) is vastly larger than $\Delta\theta^2$ (see Ref. [21] and Fig. 1), which is equivalent of high activation energies of the nucleation process. In this case it is natural to approximately evaluate the integral in equation (16) by the familiar Laplace method [22,23]. How to find a point of maximum supercooling within a mush in order to apply this method will be our initial concern. We set derivative $\Delta\theta'(z)$ in (5) equal to zero then we solve the differential equation for $\varphi(z)$ obtained in this manner:

$$\frac{b_2+\varphi}{b_3+\varphi} + b_4\frac{1}{(1-\varphi)^{2-k}}\frac{\mathrm{d}\varphi}{\mathrm{d}z} = 0.$$

As a result, we come to the following condition for point v where the constitutional supercooling attains its maximum

$$\begin{aligned} v &= \Sigma(\varphi) \\ &= -\frac{b_4}{1-k}\frac{1}{(1-\varphi)^{1-k}}\left[1+\frac{b_3-b_2}{b_2-1}F\left(k-1,1,k;\frac{1-\varphi}{b_2-1}\right)\right] \\ &\quad + \frac{b_4}{1-k}\left[1+\frac{b_3-b_2}{b_2-1}F\left(k-1,1,k;\frac{1}{b_2-1}\right)\right], \end{aligned} \tag{17}$$

where $F(\alpha,\beta,\gamma;x) = 1+\sum_{k=1}^{\infty}\frac{(\alpha)_k(\beta)_k}{(\gamma)_k}\frac{x^k}{k!}$ is the hypergeometric function [24].

Keeping only the principal term of the asymptotic expansion of integral in (16), we have (see, among others, [22,23])

$$\varphi(z) = a(v)\cdot w(z,v),$$

$$a(v) = \frac{4\pi}{3}\frac{I_*}{V}\sqrt{-\frac{\pi}{p}\frac{\Delta\theta^3(v)}{\Delta\theta''(v)}}\exp\left(-\frac{p}{\Delta\theta^2(v)}\right). \tag{18}$$

Expression (18) shows that $\varphi(v)$ vanishes (since $w(v,v) = 0$). Since function $\varphi(z)$ decreases (it is easily seen by differentiation of (16)) $\varphi(z) \approx 0$ at $v \leqslant z \leqslant 0$.[1] Keeping in mind the latter we get from (5)

$$\Delta\theta(z) = -g_1 z, \quad v \leqslant z \leqslant 0. \tag{19}$$

Substituting the linear supercooling in the form of (19) into Eq. (16) at $z = v$, we find φ at point v:

$$\varphi(v) = \frac{4\pi}{3}\frac{I_*}{V}\int_v^0\left(\sqrt{\frac{1}{q^2}+\frac{g_1}{q}\frac{\beta_*}{V}(v^2-\zeta^2)}-\frac{1}{q}\right)^3 \times \exp\left(-\frac{p}{g_1^2}\frac{1}{\zeta^2}\right)\mathrm{d}\zeta.$$

Further, substitution of $\varphi(v)$ into expression (17) gives the following transcedental equation for point v of maximal supercooling

$$v = \Sigma(\varphi(v)). \tag{20}$$

A non-trivial root of this equation corresponds to the coordinate of the maximal supercooling point in a mush (we do not consider root $v = 0$ because this case contradicts the boundary condition $\Delta\theta(0) = 0$ meaning absence of supercooling at the mush/liquid interface).

The second derivative $\Delta\theta''(v)$ entering in denominator of $a(v)$ from (18) turns to zero. To remedy this, we again calculate integral (16) by the Laplace method within interval $-h \leqslant z \leqslant v$ for the maximum boundary point $z = v$ [23]. The result is

$$\varphi(z) = b(v)\cdot w(z,v),$$

$$b(v) = -\frac{4\pi}{3}\frac{I_*}{V}\frac{v^3}{2p}g_1^2\exp\left(-\frac{p}{(g_1 v)^2}\right).$$

Thus, the solid fraction $\varphi(z)$ within a mush takes the form

$$\varphi(z) = \begin{cases} 0 & \text{for } v \leqslant z \leqslant 0, \\ b(v)\cdot w(z,v) & \text{for } -h \leqslant z < v. \end{cases} \tag{21}$$

Now let us rewrite Eq. (5) in terms of variable x_v

$$x_v = x(z) - x(v) = \frac{\beta_*}{V}\int_z^v \Delta\theta(\xi)\mathrm{d}\xi,$$

$$\frac{\mathrm{d}}{\mathrm{d}z} = \frac{\mathrm{d}x_v}{\mathrm{d}z}\frac{\mathrm{d}}{\mathrm{d}x_v} = -\frac{\beta_*}{V}\Delta\theta\frac{\mathrm{d}}{\mathrm{d}x_v}. \tag{22}$$

As a result, we conclude that the constitutional supercooling inside the mushy layer part $-h \leqslant z \leqslant v$ is governed by equation

$$\Delta\theta(x_v)\cdot\Delta\theta'(x_v) = -c_1\frac{1}{(1-\varphi)^{2-k}}\frac{\mathrm{d}\varphi}{\mathrm{d}x_v}\Delta\theta(x_v) + c_2\frac{b_2+\varphi}{b_3+\varphi}, \tag{23}$$

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[1] Strictly speaking, $\varphi(z) < 0$ for $v < z < 0$. However, from the physical meaning of φ and approximate Laplace method, we conclude that $\varphi(z) \approx 0$ within this interval.

where $c_1 = b_4/b_1$, $c_2 = V/(\beta_* b_1)$, $\varphi = \varphi(x_v) = bw(x_v)$, $w(x_v) = (\sqrt{1+2qx_v} - 1)^3/q^3$. Changing z from v to $-h$ we see that x_v varies from *0* to a certain point x_h. Putting $z = v$ (or $x_v = 0$) in (19) we find the boundary condition $\Delta\theta(0) = -g_1 v$ required to solve Eq. (23). Thus, the moving boundary problem under consideration is reduced to the first-order differential equation (23) for the constitutional supercooling supplemented by the aforementioned boundary condition (Cauchy's Problem for the Abelian equation). This equation can be easily integrated numerically.

Equating the liquidus temperature and the temperature determined at the solid/mush boundary, we get the mushy layer thickness h. This implies that $\Delta\theta(x_h) = 0$. Substitution of this condition into Eq. (23) leads to expression $(b_2 + \varphi)/(b_3 + \varphi) = 0$. This equality is ruled out for any thermophysical parameters ($\varphi \geqslant 0$, $b_2 > 0$, $b_3 > 0$). To overcome this difficulty, we take $\varphi = 1$ at $x_v = x_h$. The latter means that the mushy layer material is purely solid at the solid/mush boundary. This fact completely corresponds to the bulk crystallization theory (which is used here for kinetic mechanisms of crystal growth) developed in [18]. In this case, x_h is easily determined by equation $b \cdot w(x_h) = 1$, whence it follows that

$$x_h = \frac{1}{2q}\left((b^{-3}q + 1)^2 - 1\right).$$

The spatial coordinate z as a function of x_v is found from (22) as

$$z = z(x_v) = v - \frac{V}{\beta_*}\int_0^{x_v} \frac{\mathrm{d}\xi}{\Delta\theta(\xi)}. \tag{24}$$

Thus, the constitutional supercooling in a mushy layer is completely found. The functional dependence $\Delta\theta(z)$ for $v \leqslant z \leqslant 0$ is determined by Eq. (19) and, for $-h \leqslant z \leqslant v$, it is given in parametric representation as $\Delta\theta = \Delta\theta(x_v)$, $z = z(x_v)$ in accordance with Eqs. (23) and (24), where x_v is changed between *0* and x_h. Fig. 1 illustrates how the constitutional supercooling $\Delta\theta$ depends on the spatial coordinate z in accordance with the theory under consideration. It is seen that the supercooling increases as a linear function in the vicinity of the mush/liquid boundary ($v \leqslant z \leqslant 0$), where $\varphi \approx 0$ and nucleation and crystal growth processes are almost absent (here we keep in mind increasing with respect to the distance from the mush/liquid interface but not in the sense of z). When the supercooling attains its maximum, newly born solid elements will intensively grow. As a result, their latent heat approximately compensates the constitutional supercooling. Further, the supercooling practically vanishes within the most part of the mushy layer.

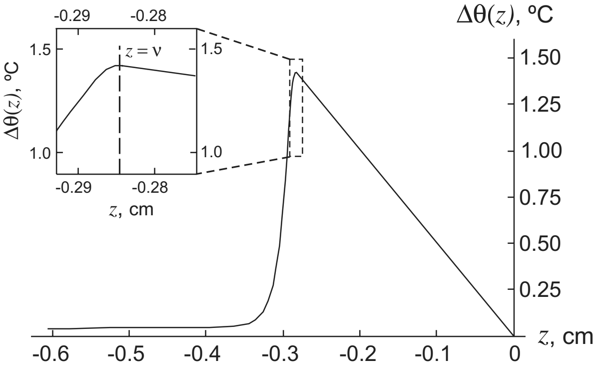

Fig. 1. The functional dependence of the constitutional supercooling in a mushy layer of the spatial coordinate ($b_1 = 0.2$ (°C)$^{-1}$, $b_2 = 2$, $b_3 = 2$, $b_4 = 5.4$ cm, $k = 0.1$, $q = 5 \times 10^4$ cm^{-1}, $p = 10$ (°C)^2, $\beta_*/V = 2 \times 10^4$ (°C)$^{-1}$, $I_*/V = 2 \times 10^4$ cm^{-4}).

5. Discussions

Fig. 2 demonstrates function $\varphi(z)$ in according with expression (21). Comparing the model under consideration and the quasiequilibrium model solved by Alexandrov [10,11], where the linear liquidus equation holds true within a mush, one can readily see well-marked differences. So, for example, a point of inflexion is enlarged in Fig. 2. From this figure we notice how the solid fraction, φ, tends to unity as the spatial coordinate approaches to the solid/mush boundary (analytically, this fact is proved by deducing expression (24)). Let us pay our attention to Eq. (4) for solute concentration. The theory under consideration is in contradiction with our common sense at a glance because $\sigma \to \infty$ when $\varphi \to 1$. To explain the latter let us pay our attention to expression (4) which describes the solute concentration over the *liquid phase* in a mush. By this is meant that the impurity amount in the liquid fraction of a mushy layer is $\Sigma = (1-\varphi)\cdot\sigma = \sigma_0\cdot(1-\varphi)^k$. This implies, that the total amount of impurity tends to zero as $\varphi \to 1$. It seems quite natural: zero volume is free of material.

From the mathematical point of view the problem under study is completely solved. However, as noted above, the kinetic theory of nucleation and crystal growth under question is physically correct if the solid fraction is less than its critical value, that is, $\varphi < \varphi_{\mathrm{crit}} < 1$. In other words, it means that our solutions are suitable only if $z > z_{\mathrm{crit}}$, where z_{crit} corresponds to φ_{crit}. In order to describe the regime for $-h < z < z_{\mathrm{crit}}$, a kinetic theory taken into consideration agglomeration and recrystallization mechanisms (principal for final stages of bulk crystallization) must be used [13]. However, we suggest another approach. The well-known

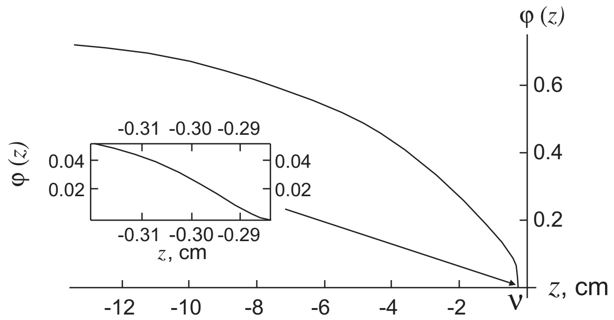

Fig. 2. The bulk fraction of crystals $\varphi(z)$ in a mushy layer ($v = -0.28$ cm).

theory of the quasiequilibrium mushy layer, where the constitutional supercooling is negligible (e.g. [1,2,8,10–12]) can be used for vanishing supercoolings and corresponding values of $z < z_{\mathrm{eq}}$ (see Fig. 1, where $\Delta\theta \approx 0$ if $z \leqslant z_{\mathrm{eq}} \approx -0.35$ cm). Thus, the non-equilibrium mushy layer is conditionally divided into two parts (see Fig. 3). The constitutional supercooling is essentially non-zero value within the first of these parts adjoining to the melt ($z_{\mathrm{eq}} \lesssim z < 0$) while it is more or less entirely compensated by the latent heat of solidification, which is released during crystallization process, within the second of them, $-h < z \lesssim z_{\mathrm{eq}}$, adjoining to the crystal. This circumstance enables us to use the quasiequilibrium theory suggested in [7,8] within the second region. The first region is also divided into two parts (see Figs. 1 and 3): solid phase elements practically absent ($\varphi \approx 0$) within the region adjacent to the melt ($\nu \leqslant z \leqslant 0$), which corresponds to the linear supercooling in accordance with (19), whereas, within the other region ($z_{\mathrm{eq}} \lesssim z < \nu$), these elements undergo intensive growth, which compensates the constitutional supercooling.

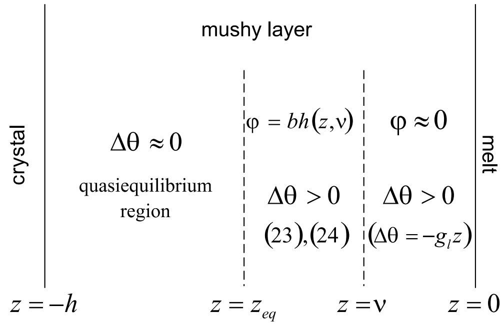

Fig. 3. A structure of non-equilibrium mushy layer.

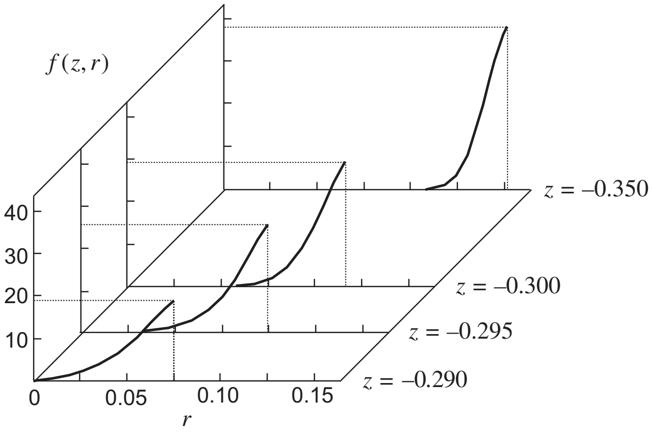

Fig. 4. Plot of $f(z,r)$ (cm^{-4}) as a function of r (cm) for $z = -0.29$, -0.295, -0.3 and -0.35 cm.

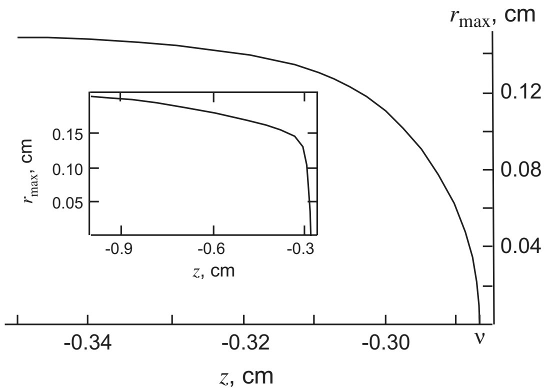

Fig. 5. Plot of $r_{\max}$ vs. z in accordance with Eq. (25).

Fig. 4 demonstrates the radial density distribution function of solid particles in a mushy layer for $z = -0.29$, -0.295, -0.3 and $z = -0.35$ cm. The maximum radius of crystals in a mushy layer can be easily found by equating the argument of the Heaviside function in (14) to zero. The obtained quadratic equation gives

$$r_{\max} = (\sqrt{1 + 2qx_{\nu}} - 1)/q. \tag{25}$$

Fig. 5 illustrates the maximum radius of crystals as a function of the spatial coordinate. With reference to Fig. 5, it can be seen that decreasing the constitutional supercooling from the mush/liquid boundary in $-z$ direction the growth rate of maximum radius decreases too. An enlargement of this behavior is clearly seen in Fig. 5. If $z \lesssim -0.35$ cm, where the supercooling tends to zero accordingly to Fig. 1, function $r_{\max}$ increases much slowly in comparison with interval $-0.35 < z < \nu$, where this function increases rather abruptly (here, as before, we keep in mind increasing with respect to the distance from the mush/liquid interface but not in the sense of z). This result immediately follows from Eq. (7), which shows that the growth rate of particles is directly proportional to the constitutional supercooling $\Delta\theta$.

6. Concluding remarks

The present study is concerned with directional solidification processes of binary melts with special attention to kinetic and growth mechanisms of solid particles treated on the basis of the bulk crystallization theory [13]. The model under consideration consists of integro-differential equations (1), (2), (11)–(13) supplemented by corresponding boundary conditions. This model is solved analytically on the basis of original and reasonable suggestions and hypotheses. In particular, the constitutional supercooling (Fig. 1), the solid fraction (Fig. 2) and the radial density distribution function of solid particles in a mushy layer (Fig. 4) are found. Unfortunately, the kinetic theory of nucleation and crystals growth under question imposes the restriction that the obtained solutions are inapplicable for sufficiently large values of φ. However, our approach for the first time allows to understand the physical structure of a mushy layer and its possible properties keeping in mind that the constitutional supercooling does not disappear.

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