Unidirectional solidification of binary melts from a cooled boundary: analytical solutions of a nonlinear diffusion-limited problem

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Abstract
A model is presented that describes nonstationary solidification of binary melts or solutions from a cooled boundary maintained at a time-dependent temperature. Heat and mass transfer processes are described on the basis of the principles of a mushy layer, which divides pure solid material and a liquid phase. Nonlinear equations characterizing the dynamics of the phase transition boundaries are deduced. Approximate analytical solutions of the model under consideration are constructed. A method for controlling the external temperature at a cooled wall in order to obtain a required solidification velocity is discussed.

1. Introduction

Directional and bulk crystallization of liquids underlies many technologies employed in traditional and new industries (metallurgy, energy, aerospace engineering, electronics) and describes natural phenomena (formation of ice, solidification of lava-streams, crystal growth in supersaturated solutions). In spite of the extended history of the study of crystallization, many aspects of the physics of this phenomenon remain unclear. Aspects of the formation of various types of micro- and macrostructures in solids and liquids, the physical mechanisms of which remain to a large degree unclear, are of particular importance. Traditionally the study of crystallization was and is performed within the framework of the classical model, leading to the Stefan boundary value problem. In this approach it is assumed that the liquid and solid phases are separated by a clearly expressed smooth (planar, cylindrical, spherical, etc) interface between the phases, heat transfer occurs by conduction according to the Fourier law and the velocity of the crystallization front is controlled by the absorption of heat by the solid phase. The mathematical formulations corresponding to these physical models belong to the class of highly nonlinear problems with moving boundaries. In spite of the appreciable progress attained in investigating these problems, it has become clear during the past several years that this approach is limited. This is because the development of experimental data on materials with specified properties necessitates the investigation of a number of new dynamic phenomena typical of the crystallization process. These phenomena include the formation of cellular and dendritic structures and the formation of two-phase (mushy) transition regions that separate the crystal and the liquid. It has become obvious that further development of theoretical and experimental studies is impossible without investigating various instabilities responsible for the formation of crystals within the liquid and for the inception of complex structures at the phase interface.

In addition it has been currently recognized that in order to explain the real structure of solids it is necessary to take account of the actual supercooling of the liquid and the consequence of the appearance of metastability (this phenomenon, among others, is responsible for the formation of cracks and 'false bottoms' in sea-ice). This requires inclusion in the study of directional crystallization and the bulk formation of the new phase ahead of the phase transition boundary (with special attention to particle

nucleation, kinetics, cluster formation) together with the propagation of metastability waves into the liquid. Analysis of available data allows us to single out several fundamental theoretical and applied problems. Firstly, the colossal complexity of the physical problems that arise when making allowance for phase transitions requires the development of a radically new approach to constructing models of crystallization, which would include various kinds of nonlinear and molecular-kinetic phenomena. Important roles are played by nucleation, fluid flows, convection and evolution of a new phase in a metastable medium, which in themselves require the refinement of established approaches and the development of new ones. Secondly, this gives rise to the need for mathematical formulation of the corresponding mathematical models, which requires the establishment of new classes of crystallization problems and the development of methods (analytical and numerical) to investigate them.

Transition from metastability to thermodynamic stability occurs when particles of the new phase grow on fluctuation-generated nuclei or on impurities serving as crystallization sites. Whereas at the initial stage of the process it is possible to regard the individual particles as being independent of one another, as the transition progresses physical nonlinearity, caused by the effect of the cluster of the growing particles on the metastability level of the surrounding matrix phase, i.e. on the supercooling, becomes substantial. The dynamics of the variation of the properties of the evolving two-phase (mushy) mixture at this stage is important not only from a theoretical but also an applied point of view. This applies particularly to crystallization from supercooled liquids or from supersaturated solutions, where quite frequently the bulk of nuclei of the new phase are supplied by fluctuations, whereas the contribution of impurities as solidification sites is relatively small [1]. Thus, this stage controls the size distribution in the products obtained in certain types of crystallizers and granulators [2, 3]. The rate of formation of the solid particles has a decisive effect on the structure of the two-phase zone at the phase interface and thus also on the physical and mechanical properties of the produced materials. The available analytic results on the evolution of the polydisperse phase in pure systems, i.e. in systems not containing heterogeneous nuclei, pertain either to the initial or to the concluding stages of phase transition [4, 5]. Studies of the first stage (nucleation), which are usually based on the kinetic theory of nucleation [6–9], are normally based on the assumption of independence of individual nuclei. The second stage (recondensation of particles of the new phase) is analysed on the basis of the Lifshits–Slezov model [10, 11], which relies substantially on the assumption that the appearance of new nuclei can be neglected. The concluding stage of bulk crystallization was analysed for cases when one of the particle-coarsening mechanisms—agglomeration or Ostwald ripening—predominates [10–12]. However, these two mechanisms cannot always be identified in 'pure form' [13, 14]. On the other hand, it is important to investigate their combined effect for the following reasons. The supercooling decreases at the concluding stage of bulk crystallization and tends to zero, whereas the radius of the critical nucleus increases. As a result, fine crystals vanish,

while large crystals continue to grow. Often, this process predominates and can be described by means of the Lifshits–Slezov theory [10, 11] in which it was shown, in part, that the total number of crystals in the system decreases in inverse proportion to time, whereas the mean volume of the crystals increases in direct proportion to time. These results were verified experimentally [13]. It was suggested that this situation could be attributed to the effect of competition for space on the size of the growing crystals [14, 15]. It was found that agglomeration and Ostwald ripening make a contribution of the same order of magnitude to the coarsening of particles [16, 17] at the concluding stage of breakdown of the metastable state. The interaction between these two mechanisms was studied recently [18]. This literature survey on the influence of particles at different stages of crystallization is certainly incomplete. A more detailed survey is given in [18].

A number of important contributions to the study of these problems have been made previously. Ivantsov [19] has demonstrated that, under certain conditions, a region of impurity-induced (constitutional) supercooling, i.e. one in which the temperature is lower than the temperature of the phase transition, forms in the melt. Subsequent to this, a relationship between this phenomenon and the structure of the solid and liquid phases was rather rapidly recognized, which has brought about intensive studies of the crystallization dynamics. Mathematical models of crystallization are complicated by the need to apply boundary conditions at solid/liquid interfaces which are evolving with time and whose positions must be found as part of the calculation. The case of a pure melt being cooled by conduction of heat to its boundaries is relatively straightforward since the geometry of the solidification front is similar to that of the bounding walls [20]. Such so-called 'Stefan' problems have been solved completely in some simple geometries. For example, solidification from a plane wall [21] and the inward solidification of cylinders and spheres [22, 23] have been considered. However, if a pure melt is supercooled (has a temperature below its freezing point), so that latent heat is conducted away from the solidification front through the liquid, then the solidification front becomes extremely convoluted and forms intricate branching patterns [24]. Snowflakes provide a common example of this phenomenon. When the liquid is an alloy (a mixture of two or more components) such behaviour is commonplace even when the liquid is not initially supercooled. At present, analytical techniques cannot follow the evolution of such convolutions far beyond initial perturbations from a flat interface, though important results have been obtained through the use of high-speed computers [25] and boundary-layer models [26]. However, for many applications, including metallurgy [27], solidification in magma chambers [28] and the structure of the Earth's inner core [29, 30], it is the gross features of the solid–liquid matrix which form as a result of the convolutions. The matrix or region of mixed phase is termed a 'mush' or 'mushy layer'. By treating the mush as a new single phase, and the macroscopic envelope of the convoluted solid as a phase boundary, it is necessary to follow the evolution of two-phase boundaries:

the solid/mush interface and the mush/liquid interface. Hills *et al* [31] developed a full set of thermodynamic equations for a mushy zone, and solved a much-reduced set of them approximately for the constrained growth of a binary alloy. Also, these model equations were solved approximately by Fowler [32]. Recently, exact analytical solutions have been constructed by Alexandrov [33–35]. Constrained growth, in which the interfaces are supposed to advance at a prescribed constant velocity, is applicable to industrial crystal pulling (Czochralski growth) but not to many natural systems. Further, Huppert and Worster [36] formulated a simple mathematical model of the mushy layer based on considerations of global conservation relationships. Its predictions agreed well with their observations of ice growing at a plane boundary from aqueous solutions of various salts. The model is particularly easy to compute. However, it relies on various assumptions (particularly that the solid fraction is constant throughout the mush) whose limits of validity are difficult to assess. More general sets of equations have been proposed by Worster [37] based upon simple considerations of local heat and mass balances. It is known that the diffusion flux determines the solute gradient in the liquid at a given growth rate and, consequently, determines the value of constitutional supercooling. However, since the liquid temperature gradient is often high, thermodiffusion (the Soret effect) should be considered as well. In many cases, thermodiffusion may have a strong dependence on composition. In particular, for dilute solutions, the thermodiffusion flux is proportional to the mean concentration [38]. Taking into account the latter, Alexandrov and Aseev developed a set of equations for a mushy layer with special attention to the Soret effect and temperature-dependent diffusivity [39, 40]. Furthermore, natural convection is of particular interest. This phenomenon complicates the process and, for example, leads to the formation of 'chimneys', which are narrow, dendrite-free regions that form within the mushy layer as a result of convection. This striking phenomenon is known to occur within solidifying alloys [41], where it is responsible for undesirable material properties; within sea-ice [42], where it has a significant effect on the ocean dynamics; within magma chambers [43], where it influences mineral deposits; and it may occur at the Earth's inner–outer core boundary [29, 44]. When the convection is sufficiently strong, the solute-rich material that flows out of the mushy layer locally depresses the melting temperature, redissolving some of the dendrites is notoriously difficult to compute. The growth of dendrites in metastable surroundings has been widely studied (see, among others, [45, 46]).

It hardly needs saying that a full survey of the literature and main results on directional and bulk crystallization is impossible. Let us also emphasize in conclusion that analytical results of nonlinear moving boundary problems are found for steady-state and self-similar processes where governing equations and boundary conditions are dependent only on a spatial or scaled variable, that is, they are ordinary differential equations and boundary conditions. The situation changes drastically in the case of real solidification processes met in practical and natural conditions when, generally speaking, the temperature and concentration fields are functions of
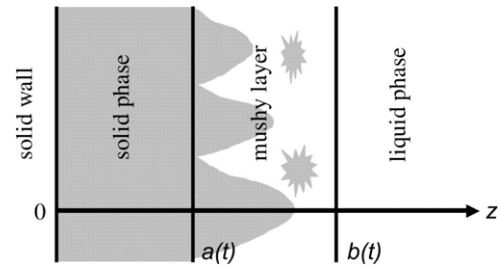

Figure 1. A scheme illustrating the process under consideration.

several time-and space-independent variables. The goal of this study is to develop the theory of nonstationary binary melt solidification from a cooled boundary with a mushy layer in the spirit of [47, 48].

2. Governing equations for a mush

We seek a description of a mushy layer that is independent of the precise morphology of the growing solid phase. In other words, we consider the model of a quasiequilibrium mushy layer when the constitutional supercooling is completely compensated by the latent heat released by growing crystals (see, among others, [18, 33–35]). The mush is thus treated as a continuum, and its physical properties are taken to be functions of the local volume fraction of solid φ. Since the solid fraction can vary with space and time, the physical properties of the mush are non-constant. The solid, mushy and liquid regions are divided by the phase transition boundaries $a(t)$ and $b(t)$ which move to deeper zones of the solid phase due to the external cooling of the boundary $z = 0$ (figure 1). Function $T_0(t)$, which describes time variations in the external (atmospheric) temperature determined at $z = 0$, is known. Let us describe solidification within the framework of the Stefan-type mushy layer model completely ignoring diffusion processes. Analysis of the observations shows that, at each time moment, the temperature profile in solid phase $T_s(z, t)$ can be approximated by a linear function of spatial coordinate z (see, for example, [49–51])

$$T_s(z, t) = T_0(t) + C_1(t)z, \qquad 0 < z < a(t), \qquad (1)$$

where $C_1(t)$ is a certain function of time. Based on the same data, we shall assume that the temperature profile in a two-phase zone, $T_m(z, t)$, is a linear function of coordinate z

$$T_m(z, t) = T_1(t) + T_2(t)z, \qquad a(t) < z < b(t). \qquad (2)$$

Here, functions $T_1(t)$ and $T_2(t)$ are found from the solution of the problem. Let us especially emphasize that linearity of temperature $T_m(z, t)$ means not only that the time of significant extension of the zone is much greater than the relaxation time of the temperature field, but also that variations in the solid phase of the zone are small (the latter statement is discussed in [47], for example).

Taking into account that the diffusion coefficient D is much smaller than the coefficient of thermal conductivity, we

shall write the equation of mass balance in a two-phase zone in the form [52, 53]

$$\frac{\partial}{\partial t}[(1-\varphi)C_m] + kC_m\frac{\partial \varphi}{\partial t} = 0, \qquad a(t) < z < b(t), \quad (3)$$

where $C_m(z,t)$ is the impurity concentration and k is the impurity distribution coefficient (k represents the ratio of the solute concentration in the solid and liquid phases at the phase transition boundary). We use expression (3) as the simplest approximation comprising the effect of impurity accumulation at the moving phase transition boundary (the key feature for a constitutionally supercooled mushy layer). Mathematically, this law follows from the differential equation describing conservation of impurities if $D = 0$.

　　We shall consider that the two-phase zone is in thermodynamic equilibrium. Therefore, the temperature and concentration of impurities are related by the liquidus equation

$$T_m(z,t) = T_p - mC_m(z,t), \qquad a(t) < z < b(t), \quad (4)$$

where m is the liquidus slope determined from the phase diagram and T_p is the freezing point at $C_m = 0$. We shall consider the case when the temperature field in the liquid phase is constant T_b at $z > b(t)$. If this is really the case, the impurity concentration at the phase transition boundary $z = b(t)$ can be found from equation (4).

　　The mass and heat balance and continuity boundary conditions applied at the two interfaces can be written in the form (see, among others, [18, 37])

$$\varphi = \varphi_a, \qquad T_s = T_m, \qquad z = a(t), \quad (5)$$

$$L_V(1-\varphi_a)\frac{da}{dt} = k_s\frac{\partial T_s}{\partial z} - F(\varphi_a)\frac{\partial T_m}{\partial z}, \qquad z = a(t), \quad (6)$$

$$C_m\frac{da}{dt}(1-k) + D\frac{\partial C_m}{\partial z} = 0, \qquad z = a(t), \quad (7)$$

$$\varphi = \varphi_b, \qquad T_m = T_b, \qquad z = b(t), \quad (8)$$

$$L_V\varphi_b\frac{db}{dt} = F(\varphi_b)\frac{\partial T_m}{\partial z}, \qquad z = b(t), \quad (9)$$

where φ_a and φ_b are the local volume fractions of solid determined at boundaries $a(t)$ and $b(t)$, respectively, L_V is the latent heat parameter, k_s and k_1 are the thermal conductivities of the solid and liquid phases. The thermal properties of the mush are assumed to be volume-fraction-weighted averages of the properties of the individual phases so that

$$F(\varphi) = k_1(1-\varphi) + k_s\varphi. \quad (10)$$

Expression (10) gives exact results for a laminated medium when there is no component of the heat flux normal to the planes of the laminates (the validity of (10) is also discussed by many authors; see, among others, [37, 54, 55]).

　　It must be emphasized that the mass balance condition at $z = b(t)$, analogous to the boundary condition (7), is absent within the framework of our model. This is due to the fact that some variations in the temperature gradient at $z = b(t)$ on the mush side of the interface (constant temperature in the solid) leads to corresponding variations in the concentration gradient

at $z = b(t)$ and, therefore, to variations in the thickness of the mushy layer in accordance with the criterion for constitutional supercooling (this condition holds for the mushy layer and its boundaries), which is

$$\frac{\partial T_m}{\partial z} = -m\frac{\partial C_m}{\partial z}.$$

　　Physically, a decrease in the temperature within a boundary layer in the solid phase causes the crystallization process, which is in progress until the local salinity attains its equilibrium value for a given temperature.

3. Results

Integrating equation (3) and taking into account expressions (2), (4) and (8), we come to the solid phase distribution within the mushy layer

$$\varphi(z,t) = 1 - (1-\varphi_b)\left[\frac{T_p - T_b}{T_p - T_1(t) - zT_2(t)}\right]^\alpha,$$
$$a(t) < z < b(t), \quad (11)$$

where $\alpha = (1-k)^{-1}$. Substitution of equations (1), (2) and (4) into the boundary conditions (5)–(9) gives

$$C_1(t) = \frac{L_V}{k_s}(1-\varphi_a)\frac{da}{dt} + \frac{F(\varphi_a)}{k_s}T_2(t), \quad (12)$$

$$\{T_2(t)[b(t) - a(t)] + T_p - T_b\}(1-k)\frac{da}{dt} = DT_2(t), \quad (13)$$

$$T_0(t) + C_1(t)a(t) = T_b + T_2(t)[a(t) - b(t)], \quad (14)$$

$$T_2(t) = \frac{L_V\varphi_b}{F(\varphi_b)}\frac{db}{dt}, \quad (15)$$

$$T_1(t) = T_b - b(t)T_2(t), \quad (16)$$

$$\varphi_a(t) = 1 - (1-\varphi_b)\frac{(T_p - T_b)^\alpha}{\left\{T_p - T_b + [b(t) - a(t)]\frac{L_V\varphi_b}{F(\varphi_b)}\frac{db}{dt}\right\}^\alpha}. \quad (17)$$

Substituting (15) into (13) and combining (12), (14) and (15), we arrive at two nonlinear equations for the determination of the phase transition boundaries

$$\left\{\frac{L_V\varphi_b}{F(\varphi_b)}\frac{db}{dt}[b(t) - a(t)] + T_p - T_b\right\}(1-k)\frac{da}{dt}$$
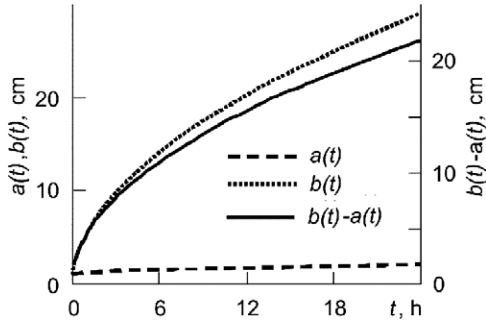$$= D\frac{L_V\varphi_b}{F(\varphi_b)}\frac{db}{dt}, \quad (18)$$

$$\frac{L_V}{k_s}(1-\varphi_b)(T_p - T_b)^\alpha a(t)\left[\frac{da}{dt} + \frac{k_s\varphi_b}{F(\varphi_b)}(K-1)\frac{db}{dt}\right]$$
$$\times \left\{T_p - T_b + [b(t) - a(t)]\frac{L_V\varphi_b}{F(\varphi_b)}\frac{db}{dt}\right\}^{-\alpha}$$
$$= T_b - T_0(t) - \frac{L_V\varphi_b}{F(\varphi_b)}b(t)\frac{db}{dt}, \quad (19)$$

where $K = k_1k_s^{-1}$.

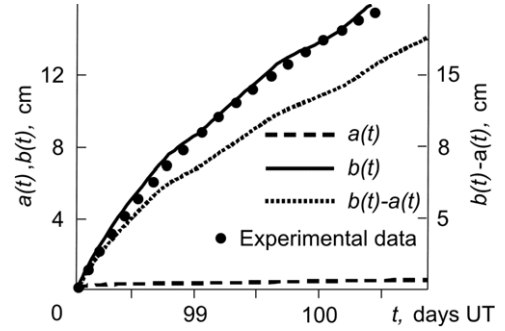　　Let us consider the case when

$$T_p - T_b \ll \frac{L_V\varphi_b}{F(\varphi_b)}[b(t) - a(t)]\frac{db}{dt}, \qquad a(t) \ll b(t)$$

Figure 2. Mushy layer coordinates and thickness for set I, $a(0) = 1$ cm, $b(0) = 2$ cm, $m = 2.65\,°C\,wt\%^{-1}$, $T_0 = 1505\,°C$, $\varphi_b = 0.2$.

Figure 3. Mushy layer coordinates and thickness for set II, $a(0) = b(0) = 0$, $\varphi_b = 0.5$, $T_0(t)$ is taken from [49, 57] for buoy 5, $m = 0.052\,36\,°C\,psu^{-1}$. The time origin corresponds to 02:21, day 98 UT. Circles represent experimental data [49, 57].

Table 1. Parameter values used for the two sets of results.

Property	Set I	Set II	Units
k	0.68	0	—
T_p	1529.5	0	°C
L_V	3398.5	73.37	cal cm^{-3}
D	5×10^{-5}	1.2×10^{-5}	cm^2 s^{-1}
k_1	0.1	1.337×10^{-3}	cal s^{-1} cm^{-1} °C^{-1}
k_s	0.177	4.848×10^{-3}	cal s^{-1} cm^{-1} °C^{-1}
T_b	1528	-2	°C

and the left-hand side of equation (19) is negligible in comparison with the right-hand side. This situation is typical for many natural systems such as binary alloys and solutions. Taking into consideration these strong inequalities, we come from (18) and (19) to exact analytical expressions for the phase transition boundaries

$$a(t) = \frac{D}{1-k} \int_0^t \frac{d\tau}{b(\tau)} + a(0), \qquad (20)$$

$$b(t) = \left\{ \frac{2F(\varphi_b)}{L_V \varphi_b} \int_0^t [T_b - T_0(\tau)]\,d\tau + b^2(0) \right\}^{1/2}, \quad (21)$$

where $a(0)$ and $b(0)$ are initial coordinates of interfaces. Equations (20) and (21) demonstrate the influence of time dispersion on the dynamics of the process. As was expected, the law of motion for both boundaries of the zone becomes self-similar (coordinates $a(t)$ and $b(t)$ are proportional to the square root of time) at constant temperature T_0 [56]. If the external temperature $T_0(t)$ undergoes different time variations, the phase transition boundaries lie between two self-similar regimes, which correspond to the maximum $T_{0\,max}$ and minimum $T_{0\,min}$ surface temperatures observed in experiments. Thus, for the boundary mushy layer–liquid phase, we have

$$\left[\frac{2F(\varphi_b)}{L_V \varphi_b}(T_b - T_{0\,max})t + b^2(0) \right]^{1/2} \leqslant b(t)$$

$$\leqslant \left[\frac{2F(\varphi_b)}{L_V \varphi_b}(T_b - T_{0\,min})t + b^2(0) \right]^{1/2}.$$

Figures 2 and 3 demonstrate a dynamics of interfaces calculated on the basis of equations (20) and (21) for the Fe–Ni alloy and the salt solution (physical properties are listed in table 1). The solid phase–mushy layer interface lags behind the
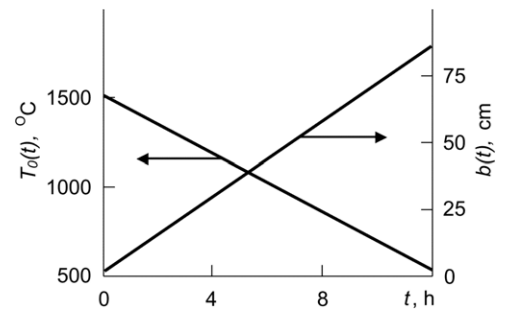
Figure 4. External temperature and phase transition boundary as functions of time.

mushy layer–liquid phase interface by virtue of the fact that the process of formation of the solid phase is hampered within the mushy layer by a high content of solid (all of the impurities rejected by the solid phase lattice are initially retained within the interstices of a layer of solid material).

The nonlinear set of equations (18) and (19) has another asymptotic solution. Formally equating the left-hand side of (19) to zero, we obtain

$$a(t) = Bb(t) + B_1, \qquad B = \frac{k_s \varphi_b(1-K)}{F(\varphi_b)}, \qquad (22)$$

$$B_1 = a(0) - Bb(0).$$

Substitution of (22) into (18) gives a quadratic equation for $b(t)$

$$\frac{1-B}{2}b^2(t) - B_1 b(t) - \left[\frac{D}{(1-k)B} + \frac{(T_b - T_p)F(\varphi_b)}{L_V \varphi_b} \right] t$$

$$= \frac{1-B}{2}b^2(0) - B_1 b(0). \qquad (23)$$

Expressions (20), (21) and (22), (23) determine two approximate analytical solutions of equations (18) and (19) for different values of physical parameters and different magnitudes of the free parameter φ_b.

In many cases it is important to know how to change the external temperature $T_0(t)$ with the goal of obtaining the required solidification rate $v(t) = db/dt$ (for example, the goal is to realize industrial crystal pulling with a constant velocity
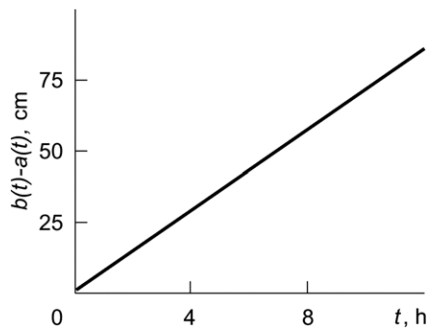
Figure 5. Mushy layer thickness as a function of time, $v = 1.952 \times 10^{-3}$ cm s^{-1}.

v_0). Substituting v_0 into (21) or equating the right-hand side of (19) to zero, we get

$$v_0 = \frac{F(\varphi_b)(T_b - T_0(0))}{L_V \varphi_b b(0)},$$

$$T_0(t) = T_b - \frac{L_V \varphi_b (v_0 t + b(0)) v_0}{F(\varphi_b)}.$$

Figures 4 and 5 illustrate functions $T_0(t)$, $b(t)$ and $b(t) - a(t)$ describing the solidification scenario from a cooled boundary with a constant velocity. This approach can be used in the case of an arbitrary function of $v(t)$. However, we will not dwell on this point for reasons of space.

Let us emphasize in conclusion that the importance of this study primarily consists of new analytical results of the nonlinear nonstationary problem of directional solidification with a mushy layer from a cooled boundary maintained at a time-dependent temperature.

Acknowledgments

References

[1] Chernov A A 1984 *Modern Crystallography III: Crystal Growth* (Berlin: Springer)
[2] Todes O M, Sebalo V A and Gol'tsiker L D 1984 *Batch Crystallization from Solutions* (Leningrad: Khimiya Publishing House)
[3] Chalmers B 1967 *Physical Metallurgy* (New York: Wiley and Chapman)
[4] Lushnikov A A and Sutuchin A G 1976 *Usp. Khim.* **55** 385
[5] Lifshits E M and Pitaevskiy L P 1979 *Physical Kinetics* (Moscow: Nauka)
[6] Volmer M and Weber A 1926 *Z. Phys. Chem.* A **119** 277
[7] Frenkel J 1955 *Kinetic Theory of Liquids* (New York: Dover)
[8] Skripov V P 1974 *Metastable Liquids* (New York: Wiley)
[9] Buyevich Yu A and Natalukha I A 1994 *Chem. Eng. Sci.* **49** 3241
[10] Lifshits I M and Slezov V V 1958 *Zh. Eksp. Tekch. Fiz.* **35** 479
[11] Slezov V V and Sagalovich V V 1987 *Usp. Fiz. Nauk* **151** 67
[12] Gardiner C W 1983 *Handbook on Stochastic Methods: for Physics, Chemistry and the Natural Sciences* (Berlin: Springer)
[13] Wagner C 1961 *Z. Electrochem.* **65** 581
[14] Arbell A J 1972 *Acta Metall.* **20** 61
[15] Margusee J A and Ross J 1984 *J. Chem. Phys.* **80** 536
[16] Brown L C 1987 *Scr. Metall.* **21** 693
[17] Wan G and Sam P 1990 *Acta Metall. Mater.* **38** 2367
[18] Buyevich Yu A, Alexandrov D V and Mansurov V V 2001 *Macrokinetics of Crystallization* (New York: Begell House)
[19] Ivatsov G P 1947 *Dokl. Akad. Nauk SSSR* **81** 179
[20] Sekerka R F 1973 Morphological stability *Crystal Growth: An Introduction* ed P Hartman (Amsterdam: North-Holland) pp 403–42
[21] Carslaw H S and Jaeger J C 1959 *Conduction of Heat in Solids* (London: Oxford University Press)
[22] Riley D S, Smith F T and Poots G 1974 *Int. J. Heat Mass Transfer* **17** 1507
[23] Soward A M 1980 *Proc. R. Soc.* A **373** 131
[24] Langer J S 1980 *Rev. Mod. Phys.* **52** 1
[25] Ungar L H and Brown R A 1984 *Phys. Rev.* B **29** 1367
[26] Ben-Jacob E, Goldenfeld N, Langer J S and Schon G 1983 *Phys. Rev. Lett.* **51** 1930
[27] Copley S M, Giamei A F, Johnson A F and Hornbecker M F 1970 *Metall. Trans.* **1** 2193
[28] Chen C F and Turner J S 1980 *J. Geophys. Res.* **85** 2573
[29] Fearn D R, Loper D E and Roberts P H 1981 *Nature* **292** 232
[30] Loper D E 1983 *Geophys. Astrophys. Fluid Dyn.* **25** 139
[31] Hills R N, Loper D E and Roberts P H 1983 *Q. J. Appl. Math.* **36** 505
[32] Fowler A C 1985 *IMA J. Appl. Math.* **35** 159
[33] Alexandrov D V 2001 *J. Cryst. Growth* **222** 816
[34] Alexandrov D V 2001 *Acta Mater.* **49** 759
[35] Alexandrov D V 2000 *Phys. Dokl.* **45** 569
[36] Huppert H E and Worster M G 1985 *Nature* **314** 703
[37] Worster M G 1986 *J. Fluid Mech.* **167** 481
[38] Van Vaerenbergh S, Garandet J P, Praizey J P and Legros J C 1998 *Phys. Rev.* E **58** 1866
[39] Alexandrov D V and Aseev D L 2005 *J. Fluid Mech.* **527** 57
[40] Alexandrov D V and Aseev D L 2006 *Comput. Mater. Sci.* **37** 1
[41] Hellawell A, Sarazin J R and Steube R S 1993 *Phil. Trans. R. Soc.* A **345** 507
[42] Eide L I and Martin S 1975 *J. Glaciol.* **14** 137
[43] Tait S and Jaupart C 1992 *J. Geophys. Res.* **97** 6735
[44] Bergman M I and Fearn D R 1994 *Geophys. Res. Lett.* **21** 477
[45] Galenko P K and Zhuravlev V A 1994 *Physics of Dendrites* (Singapore: World Scientific)
[46] Langer J S and Muller-Krumbhaar H 1978 *Acta Metall.* **26** 1681
[47] Alexandrov D V, Malygin A P and Alexandrova I V 2006 *Ann. Glaciol.* **44** 118
[48] Alexandrov D V and Malygin A P 2006 *Dokl. Earth Sci.* A **411** 1407
[49] Morison J *et al* 1993 *EOS Trans. AGU* **74** 393
[50] Martin S and Kauffman P 1974 *J. Fluid Mech.* **64** 507
[51] Alexandrov D V, Buyevich Yu A, Mansurov V V, Vabishchevich P N and Churbanov A G 1997 Computer simulation of binary melt crystallization with changeover of boundary conditions *Multiple Scale Analyses and Coupled Physical Systems: Proc. Saint-Venant Symp. (Paris, Aug. 1997)* pp 529–34
[52] Kerr R C, Woods A W, Worster M G and Huppert H E 1990 *J. Fluid Mech.* **216** 323
[53] Scheil E 1942 *Z. Metalld* **34** 70
[54] Batchelor G K 1974 *Annu. Rev. Fluid Mech.* **6** 227
[55] Buyevich Yu A and Alexandrov D V 2005 *Heat Transfer in Dispersions* (New York: Begell House)
[56] Alexandrov D V and Malygin A P 2006 *Int. J. Heat Mass Transfer* **49** 763
[57] Wettlaufer J S, Worster M G and Huppert H E 2000 *J. Geophys. Res.* **105** 1123