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QUASISTATIONARY FORMS OF CRYSTAL GROWTH IN LOCALLY NONEQUILIBRIUM DIFFUSION OF IMPURITY

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Isoconcentration forms of crystal growth are obtained in a quasistationary approximation using a model of locally nonequilibrium diffusion in high-speed solidification of a binary system. Four isoconcentration forms of growth (an elliptic paraboloid, a paraboloid of revolution, a parabolic cylinder, and a parabolic plate) are found for crystals that grow along a selected coordinate at a constant velocity. In the isothermal case of nondiffusion solidification, i.e., when the velocity of crystal growth is equal to or higher than the rate of impurity diffusion, these surfaces have an arbitrary configuration.

Introduction. Papapetrou [1] was the first to suggest a satisfactory description of the form of crystal growth by the surface of a paraboloid of revolution. A mathematical description of the growth of a paraboloid crystal was made by Ivantsov [2]. By and large Ivantsov [2-4] and subsequently Horvay and Cahn [5] found solutions for seven basic forms of crystal growth that satisfy balance conditions at the phase interface in diffusion transfer of heat or mass in the volume of the system. These solutions were obtained for quasi-equilibrium conditions of growth of isotropic crystals in a nonstationary mode (the velocity of growth decreases in proportion to the square root of time) or in motion with a constant velocity along a chosen direction (the dendrite problem). The solutions of [2-5] provided a basis for theoretical investigation of crystal growth [6-8] and further development of the theory of anisotropic dendrite growth of crystals (see, e.g., [9]).

In the study of the phenomena of high-speed solidification in the processes of quenching from the liquid state, atomization, electromagnetic levitation, and laser and electron treatment of the surface [10], there exists the problem of determining the forms of the growth and structure of the crystals and the phase and chemical inhomogeneity of the material. In these processes, conditions of quasi-equilibrium can no longer be satisfied and crystal growth occurs under significant deviations from local thermodynamic equilibrium [7, 10]. Therefore, in consideration of high-speed solidification, analysis of crystal growth [2-5] must be supplemented with the condition of local nonequilibrium.

The present work is aimed at finding a quasistationary solution that determines the forms of growth of isotropic crystals in the case of high-speed solidification of a binary system. A key feature of the suggested analysis is use of the assumption that the velocity of phase-interface motion can be comparable to the diffusion rate or even exceed it in the volume of the mother medium [11-14]. In this case, one should take into account the finite velocity of diffusion propagation of mass in a locally nonequilibrium approximation described by a hyperbolic equation of transfer [11-14].

1. Problem Formulation. We consider isothermal solidification of a binary system. As is known, the ratio of the characteristic spatial scales of diffusion l_D and heat transfer l_T is of little importance for metal alloys, $l_D/l_T = 5\cdot10^{-4}$–$1\cdot10^{-3}$, or for nonmetal binary systems $l_D/l_T \simeq 10^{-2}$. Therefore, the isothermal approximation holds for consideration of the motion of the solidification surface on diffusion scales and is limited from above by several thermal scales within the limits of which the temperature does not change substantially. We will also neglect diffusion in the solid phase, since the coefficient of diffusion in a crystal is much smaller than that in a liquid. With allowance for these assumptions, we apply the relaxation approach [15] to the description of locally nonequilibrium diffusion in high-speed solidification, $V \sim V_D$ = 0.1–10 m/sec [11-14].

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In the absence of local thermodynamic equilibrium in the concentration field, the relation between the vector of the mass flow $\vec{J}$ and the gradient ∇C of the impurity concentration C in the liquid phase has the integral form

$$\vec{J} = -\int_0^\infty D_R(t')\, \nabla C(t-t', \vec{r})\, dt' , \tag{1}$$

where t is the time; $\vec{r}$ is the radius vector of the point in the system; $D_R(t')$ is the relaxation function of the mass flow. Equation (1) allows for the case of interface motion with a high velocity when local equilibrium in the diffusion field has no time to become established and the mass flow at a point of the alloy is independent of the instantaneous value of the concentration gradient and is determined by the local prehistory of the solidification process. We represent the relaxation function $D_R(t')$ in exponential form:

$$D_R(t') = D_R(0) \exp(-t'/\tau_D) , \tag{2}$$

where $\tau_D = D/V_D^2$ is the time of local diffusion relaxation of the mass flow to its stationary state (τ_D can also be considered as the time of diffusion relaxation of a group of atoms to their equilibrium state in the local volume); V_D is the diffusion rate, i.e., the maximum velocity of diffusion propagation of concentration nonuniformities in the system (V_D can also be defined as the velocity of motion of the concentration-profile front); $D = \tau_D D_R(0)$ is the coefficient of diffusion. Substituting Eq. (2) into Eq. (1), we can obtain a generalized Fick law in the form

$$\vec{J} + \tau_D \frac{\partial \vec{J}}{\partial t} + D\nabla C = 0 . \tag{3}$$

Equation (3) is the simplest generalization of the classical Fick law $\vec{J} + D\nabla C = 0$ which can be established for $\tau_D = 0$ or in the stationary case where $\partial\vec{J}/\partial t = 0$. The evolution equation (3) allows for relaxation of the mass flow to local equilibrium and is known as the Maxwell–Kattaneo equation in the case of consideration of heat transfer in a continuous medium at a finite rate [15]. As follows from Eq. (3), the concentration gradient ∇C at a point of the system determines the vector $\vec{J}$ of the mass flow not at the same instant of time t as in the locally equilibrium approximation, but with a delay equal to the relaxation time τ_D.

Conservation of mass in the system is described by the balance equation

$$\frac{\partial C}{\partial t} + \nabla \cdot \vec{J} = 0 , \tag{4}$$

where ($\cdot$) denotes the scalar product of the vectors. In contrast to the first Fick law, which leads to a parabolic diffusion equation, relations (3) and (4) give a hyperbolic equation for the concentration:

$$\frac{\partial C}{\partial t} + \tau_D \frac{\partial^2 C}{\partial t^2} = D\nabla^2 C . \tag{5}$$

Equation (5) combines diffusion (dissipative) and wave regimes of mass transfer under locally nonequilibrium conditions. In this case, it describes the processes of mass transfer in so-called "non-Fick diffusion."

At the liquid–solid interface the condition

$$-D\nabla_{\mathrm{n}} C = (C - C_{\mathrm{s}})\, V_{\mathrm{n}} + \tau_D \frac{\partial}{\partial t} ((C - C_{\mathrm{s}})\, V_{\mathrm{n}}) , \tag{6}$$

$$C_{\mathrm{s}} = kC \tag{7}$$

holds [16, 17], where $\nabla_n C$ is the component of the gradient of impurity concentration normal to the phase interface; V_n is the normal component of the vector $\vec{V}$ of the velocity of interface motion. We take constancy of the concentration in the liquid phase

$$C|_{\infty} = C_0 \tag{8}$$

as the boundary condition at infinity.

In the quasistationary mode at a constant velocity $\vec{V}$ of interface motion, the total derivatives are zero:

$$\frac{dC}{dt} = \frac{\partial C}{\partial t} + \vec{V}\cdot\nabla C = 0\,, \tag{9}$$

$$\frac{d}{dt}\,((C - C_s)\,V_n) = \frac{\partial}{\partial t}\,((C - C_s)\,V_n) + \vec{V}\cdot\nabla\,((C - C_s)\,V_n) = 0\,. \tag{10}$$

Next, we consider the case where the concentration along the phase interface is constant. Using (9) and (10), in the quasistationary mode we obtain for Eq. (6)

$$(\nabla_n C)^2 - \frac{1}{V_D^2}\left(\frac{\partial C}{\partial t}\right)^2 = \frac{C - C_s}{D}\,\frac{\partial C}{\partial t}\,. \tag{11}$$

We find a general solution of a growth form that coincides with the isoconcentration surface. For this purpose, we consider the nonlinear partial differential equation of first order

$$\left(\frac{\partial C}{\partial x}\right)^2 + \left(\frac{\partial C}{\partial y}\right)^2 + \left(\frac{\partial C}{\partial z}\right)^2 - \frac{1}{V_D^2}\left(\frac{\partial C}{\partial t}\right)^2 = \frac{f(C)}{D}\,\frac{\partial C}{\partial t}\,, \tag{12}$$

which is the general form of Eq. (11).

2. General Solution. We find the total integral of Eq. (12) by the Lagrange–Sharpee method (see, e.g., [18], p. 264). It has the form

$$I = \frac{C_1^2 + C_2^2 + C_3^2 - C_4^2/V_D^2}{C_4}\,DF\,(C) + C_1 x + C_2 y + C_3 z + C_4 t + C_5 = 0\,, \tag{13}$$

$$F\,(C) = -\int \frac{dC}{f\,(C)}\,, \tag{14}$$

where C_i are the integration constants (i = 1, 2, 3, 4, 5). Then, the solution (13) and (14) gives a functional dependence of the concentration C on F of the form

$$C = \Phi\,(F)\,. \tag{15}$$

The function Φ in Eq. (15) must satisfy the equation of locally nonequilibrium diffusion (5) and boundary condition (11). Substitution of (15) into (5) yields

$$\frac{d^2\Phi}{dF^2} = \frac{\partial F/\partial t + \tau_D\,(\partial^2 F/\partial t^2) - D\nabla^2 F}{D\,(\nabla F)^2 - \tau_D\,(\partial F/\partial t)^2}\,\frac{d\Phi}{dF}\,. \tag{16}$$

On the solidification surface, we have $F = F_0$ and $C = C_f$. Then, it follows from (15) and (11) that

$$\frac{d\Phi}{dF}=\frac{(C_\mathrm{f}-C_\mathrm{s})}{D}\frac{\partial F/\partial t}{(\nabla F)^2-(1/V_D^2)\,(\partial F/\partial t)^2}\,. \tag{17}$$

We now find the total integral of Eq. (12), having assigned, in the solution (13), a linear relation between the arbitrary constants: $C_4 = -VC_3$ and $C_5 = -DBC_2^2/VC_3$. Then, from (13) it follows that

$$I=-\frac{C_1^2+C_2^2+(1-V^2/V_D^2)\,C_3^2}{VC_3}\,DF+C_1x+C_2y+C_3\,(z-Vt)-\frac{DBC_2^2}{VC_3}\,. \tag{18}$$

Having taken the derivatives of I with respect to C_i and having equated them to zero, from (18) we find an equation of isoconcentration surfaces in the form

$$\frac{Vx^2}{4DF}+\frac{Vy^2}{4D\,(F+B)}=\frac{DF}{V}\,(1-V^2/V_D^2)-(z-Vt)\,. \tag{19}$$

For $F = F_0$, Eq. (19) describes the solidification surface, which in the general case is a paraboloid.

We consider the mean curvature H and the related radius R ($H = 1/R$) at the peak of the paraboloid with the coordinates $x = y = 0$, $z - Vt = DF(1 - V^2/V_D^2)/V$. The mean curvature

$$H=\frac{1}{2}\left(\frac{1}{R_1}+\frac{1}{R_2}\right)=\frac{1}{2}\,\frac{\partial^2 z/\partial x^2}{(1+(\partial z/\partial x)^2)^{3/2}}\bigg|_{x=0,y=0}+\frac{1}{2}\,\frac{\partial^2 z/\partial y^2}{(1+(\partial z/\partial y)^2)^{3/2}}\bigg|_{x=0,y=0}$$

(R_1 and R_2 are the principal radii of curvature along the x and y directions, respectively) at the top of the solidification surface has the form

$$H=\frac{1}{R}=\frac{V}{4D}\,\frac{2F_0+B}{F_0\,(F_0+B)}\,. \tag{20}$$

We introduce the Peclet number $\mathrm{Pe} = VR/2D$. Then from Eq. (20) we obtain an expression for F_0 in the form

$$F_0=\frac{1}{2}\left(\mathrm{Pe}-B+(\mathrm{Pe}^2+B^2)^{1/2}\right). \tag{21}$$

With account for (19), Eqs. (16) and (17) take the form

$$\frac{d^2\Phi}{dF^2}=-\left(1+\frac{1}{2F}+\frac{1}{2\,(F+B)}\right)\frac{d\Phi}{dF}\,, \tag{22}$$

$$\frac{d\Phi}{dF}\bigg|_{F=F_0}=C_\mathrm{s}-C_\mathrm{f}\,. \tag{23}$$

Integrating Eq. (22), we find the general solution in the form

$$\Phi=A_1\,J\,(F,B)+A_2\,, \tag{24}$$

$$J\,(F,B)=\int_F^{F_\infty}\frac{\exp\,(-F')}{(F'\,(F'+B))^{1/2}}\,dF'\,, \tag{25}$$

where F_∞ corresponds to the infinite point $z = \infty$, and A_1 and A_2 are the constants of integration.

2.1. The velocity of growth is lower than the diffusion rate. We consider the case where $V < V_D$. From Eq. (19) it follows that the infinite point $z = \infty$ corresponds to $F_\infty = \infty$. Thus, we have that the function

$$J(F, B) = \int_F^\infty \frac{\exp(-F')}{(F'(F' + B))^{1/2}} \, dF' \tag{26}$$

is bounded. Allowing for boundary conditions (6)-(8) and (23), we find

$$C = \Phi(F) = (C_\mathrm{f} - C_0) \frac{J(F, B)}{J(F_0, B)} + C_0 \,, \tag{27}$$

where

$$C_\mathrm{f} = \frac{C_0}{1 - (1 - k)\, \Psi(F_0, B)} \,, \tag{28}$$

$$\Psi(F_0, B) = F_0^{1/2} (F_0 + B)^{1/2} \exp(F_0)\, J(F_0, B) \,. \tag{29}$$

It should be noted that in Eqs. (27)-(29) the functions $J(F, B)$ and $\Psi(F_0, B)$ involve the parameters F and F_0, which depend on the spatial coordinates and the factor $(1 - V^2/V_D^2)$ (see Eq. (19)). Herein lies the difference between the general solution of (19) and (27)-(29) and the classical solution found earlier for the locally equilibrium limit $V_D \to \infty$, i.e., for an infinite velocity of impurity propagation [2-5]. There also exists a fundamental difference from the classical solution [2-5] that consists in degeneration of the diffusion profile for a finite velocity $V \geq V_D$. We show this in the following subsection.

2.2. The velocity of growth is higher than or equal to the diffusion rate. We now consider the case of $V > V_D$. Then for the infinite point $z = \infty$ we have $F_\infty = -\infty$ (see Eq. (19)), and the function $J(F, B)$ is (see Eq. (25))

$$J(F, B) = -\int_{-\infty}^F \frac{\exp(-F')}{(F'(F' + B))^{1/2}} \, dF' \,. \tag{30}$$

As an analysis shows, this integral diverges. Therefore, for the function Φ to remain bounded, it is necessary to take $A_1 = 0$ in the solution (24). From boundary conditions (6)-(8) we find

$$C = \Phi(F) = C_0 \,, \quad C_\mathrm{f} = C_\mathrm{s} = C_0 \,. \tag{31}$$

In this case we have that at the phase interface the function $f(C)$ has a zero value, $f(C) = 0$, and divergence exists in integral (14), which determines $F(C)$. To solve the problem for $V \geq V_D$, we consider a method of solution of the hyperbolic equation (5) that allows one to find the solution of the three-dimensional problem for arbitrary velocities V.

We introduce the dimensionless concentration $\tilde{C} = (C - C_0)/C_0$. In accordance with the boundary condition (8) we have

$$\tilde{C}|_\infty = 0 \,. \tag{32}$$

To analyze quasistationary motion with velocity V, we convert to the variable $\tilde{z} = z - Vt$. Then, from (5) we obtain an equation describing the three-dimensional distribution of the concentration of impurity:

$$\frac{\partial^2\tilde{C}}{\partial x^2}+\frac{\partial^2\tilde{C}}{\partial y^2}+(1-V^2/V_D^2)\,\frac{\partial^2\tilde{C}}{\partial\tilde{z}^2}+\frac{V}{D}\,\frac{\partial\tilde{C}}{\partial\tilde{z}}=0\,. \tag{33}$$

The general solution of Eq. (33) can be represented in the form

$$\tilde{C}\,(x,y,\tilde{z})=\int\limits_{-\infty}^{\infty}dn\int\limits_{-\infty}^{\infty}dm\,\exp\,(inx)\,\exp\,(imy)\,f_{nm}\,(\tilde{z})\,, \tag{34}$$

where n and m are the eigenvalues that correspond to the eigenfunctions exp $(inx)/\sqrt{2\pi}$ and exp $(imy)/\sqrt{2\pi}$ of the Laplace operator in an infinite space. In accordance with (32) the function f_{nm} is zero, i.e., $f_{nm}=0$ when $\tilde{z}\to\infty$. From (33) we obtain an ordinary differential equation that determines the function $f_{nm}(\tilde{z})$:

$$(1-V^2/V_D^2)\,\frac{d^2f_{nm}}{\partial\tilde{z}^2}+\frac{V}{D}\,\frac{df_{nm}}{\partial\tilde{z}}-(n^2+m^2)\,f_{nm}=0\,. \tag{35}$$

As a result we find that the solution of Eq. (35) is

$$f_{nm}=B_1\,\exp\,(\lambda_1\tilde{z})+B_2\,\exp\,(\lambda_2\tilde{z})\,, \tag{36}$$

where

$$\lambda_1=-\frac{V}{2D\,(1-V^2/V_D^2)}\left(1-\left(1+\frac{4D\,(n^2+m^2)\,(1-V^2/V_D^2)}{V^2}\right)^{1/2}\right);$$

$$\lambda_2=-\frac{V}{2D\,(1-V^2/V_D^2)}\left(1+\left(1+\frac{4D\,(n^2+m^2)\,(1-V^2/V_D^2)}{V^2}\right)^{1/2}\right).$$

An analysis of Eq. (36) makes it possible to determine the following. When $V<V_D$, we have that $\lambda_1>0$ and $\lambda_2<0$. From the condition $f_{nm}|_{\tilde{z}\to\infty}=0$ we can find that $B_1=0$, and B_2 is determined from the boundary conditions at the phase interface (see Eqs. (6) and (7)). When $V\geq V_D$, we have that λ_1 and λ_2 are complex numbers. Here, we have that Re $\lambda_1>0$ and Re $\lambda_2>0$. It also follows from the condition $f_{nm}|_{\tilde{z}\to\infty}=0$ that $B_1=0$ and $B_2=0$. Thus, when $V\geq V_D$, we have $f_{nm}=0$. Upon passage to the dimensional concentration corresponding to (34), we obtain

$$C\,(x,y,z)=C_0\,,\quad C_{\mathrm{f}}=C_0 \tag{37}$$

irrespective of the shape of the phase interface in solidification. This result has the following physical meaning. As soon as the liquid–crystal interface moves with a velocity $V\geq V_D$, nondiffusion solidification occurs (see Eq. (37) and [16, 17, 19]). In this case, isothermal solidification of the system is limited only by the kinetics of attachment of particles (atoms and molecules) to the interface, and the surface shape can have an arbitrary macroscopic configuration in a chemically homogeneous region. Thus, according to Eq. (37), near an isoconcentration surface of arbitrary shape the concentration field is homogeneous: $C=C_0$ when $V\geq V_D$.

2.3. Comparison with the solution for a plane front. We consider degeneration of the phase interface into a plane front with $R\to\infty$. In accordance with Eq. (21), we have $F_0\to\infty$. Let $F=F_0+\xi$, where $\xi\geq 0$. Then, when $F_0\to\infty$, we can find from Eq. (19) that

$$\xi=F-F_0=\frac{V\,(z'-Vt')}{D\,(1-V^2/V_D^2)}\,, \tag{38}$$

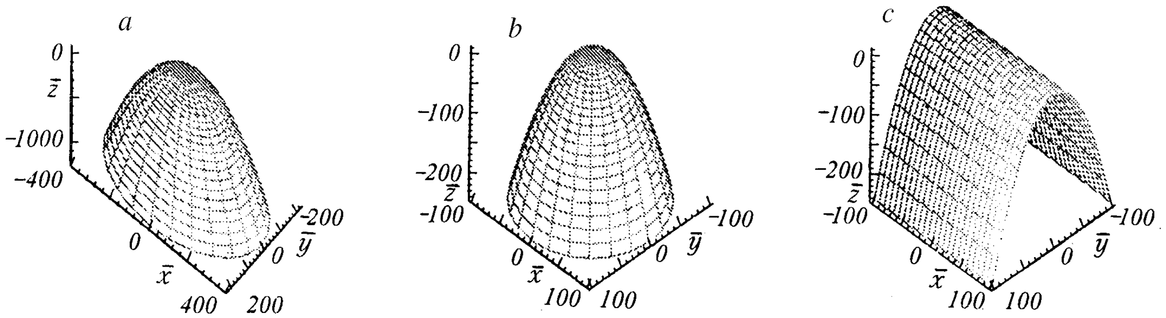

Fig. 1. Three-dimensional shapes of growing crystals for $V < V_D$ and $V/V_D = 0.5$ presented in dimensionless coordinates $\bar{z} \equiv (z - Vt)/(D/V_D)$, $\bar{x} \equiv x/(D/V_D)$, $\bar{y} \equiv y/(D/V_D)$ and corresponding to the cases: a) elliptic paraboloid with $F_0 = 5$ and $B = 10$; b) paraboloid of revolution with $F_0 = \mathrm{Pe} = 5$ and $B = 0$; c) parabolic cylinder with $F_0 = \mathrm{Pe}/2 = 5$ and $B = \infty$.

where $z' = z - z_0$ and $t' = t - t_0$ (z_0 is the position of the plane front at the instant t_0).

From Eqs. (26), (27), (37), and (38) the distribution of the concentration in front of the plane front is given by the expression

$$C = \begin{cases} (C_\mathrm{f} - C_0) \exp\left(-\dfrac{V(z' - Vt')}{D(1 - V^2/V_D^2)}\right) + C_0 , & V < V_D , \\ C_0 , & V \geq V_D . \end{cases} \tag{39}$$

When $F_0 \to \infty$ (i.e., when the radius of curvature tends to infinity, $R \to \infty$, see Eq. (21)), Eqs. (28), (29), and (37) yield an expression for the impurity concentration on a plane front:

$$C_\mathrm{f} = \begin{cases} \dfrac{C_0}{k} , & V < V_D , \\ C_0 , & V \geq V_D . \end{cases} \tag{40}$$

Thus, the result described by Eqs. (39) and (40) fully corresponds to the results of [16], where high-speed solidification with a plane front in locally nonequilibrium diffusion is studied analytically.

3. Forms of Crystal Growth. We consider special cases that follow from the solutions (19) and (26)-(29). These solutions will determine isoconcentration shapes of crystals growing with a constant velocity V in the direction of the coordinate axis z. It should be noted that according to the result found in Subsec. 2.2, in an isothermal system transition from a diffusion-limited regime to a kinetically controlled one occurs simultaneously with transition to nondiffusion solidification and motion of an arbitrary isoconcentration surface in a chemically homogeneous liquid. Therefore, in what follows we give results only for forms of growth with $V < V_D$. It is assumed for the case of $V \geq V_D$ that in an isothermal system the phase interface takes an arbitrary shape in a uniform concentration field, $C = C_0$.

3.1. Elliptic paraboloid. At finite values of F and B the general solutions (19) and (28) describe the shape of an elliptic paraboloid and the concentration of impurity on its surface for $V < V_D$ (see Fig. 1a). In the limit $V_D \to \infty$, which is a locally equilibrium approximation for the diffusion of the impurity, the solutions (19) and (27)-(29) pass to the solutions found by Ivantsov [2-4] and Horvay and Cahn [5].

3.2. Paraboloid of revolution. At $B = 0$, from Eqs. (19) and (21) we can find the equation for the shape of the phase interface, $F = F_0 = \mathrm{Pe}$. The shape is determined by the relation

$$z - Vt = \frac{R\,(1 - V^2/V_D^2)}{2}\left(1 - \frac{x^2 + y^2}{R^2\,(1 - V^2/V_D^2)}\right). \tag{41}$$

It describes the shape of a paraboloid of revolution (see Fig. 1b).

In accordance with the solutions (21), (26), and (27), the concentration field near this paraboloid is described by the equation

$$C = (C_{\mathrm{f}} - C_0)\,\frac{E_1\,(\mathrm{Pe}\,u)}{E_1\,(\mathrm{Pe})} + C_0\,, \tag{42}$$

where

$$E_1\,(x) = \int_x^\infty \frac{\exp\,(-\,s)}{s}\,ds$$

is the exponential integral function. The function u in Eq. (42) is determined by the expression Pe $u = F_+$, where F_+ is the positive root of Eq. (19) at $B = 0$. Thus, we obtain

$$u = \frac{z - Vt + ((z - Vt)^2 + (1 - V^2/V_D^2)\,(x^2 + y^2))^{1/2}}{R\,(1 - V^2/V_D^2)}\,. \tag{43}$$

At $B = 0$ and $F_0 = \mathrm{Pe}$ (see Eq. (21)), from Eqs. (28) and (29) we can find the concentration on the surface of a paraboloid of revolution in the form

$$C_{\mathrm{f}} = \frac{C_0}{1 - (1 - k)\,\mathrm{Iv}\,(\mathrm{Pe})}\,, \tag{44}$$

where

$$\mathrm{Iv}\,(x) = x\,\exp\,(x)\,E_1\,(x)$$

is the Ivantsov function [5-10].

3.3. Parabolic cylinder. When $B \to \infty$, from (19) and (21) we can find the following equation for the shape of the interface: $F = F_0 = \mathrm{Pe}/2$. This shape is defined by the equation

$$z - Vt = \frac{R\,(1 - V^2/V_D^2)}{4}\left(1 - \frac{4x^2}{R^2\,(1 - V^2/V_D^2)}\right), \tag{45}$$

which describes the surface of an infinite parabolic cylinder (see Fig. 1c).

In accordance with the solutions (21), (26), and (27), the concentration field near this cylinder is described as

$$C = (C_{\mathrm{f}} - C_0)\,\frac{\mathrm{erfc}\,((\mathrm{Pe}\,u)^{1/2})}{\mathrm{erfc}\,(\mathrm{Pe}^{1/2})} + C_0\,. \tag{46}$$

In this case, the function u is determined by the expression Pe $u = F_+$, where F_+ is the positive root of Eq. (19) when $B \to \infty$. Thus, we can obtain

$$u = \frac{z - Vt + ((z - Vt)^2 + (1 - V^2/V_D^2)\,x^2)^{1/2}}{R\,(1 - V^2/V_D^2)}\,. \tag{47}$$

With account for the solutions (21), (28), and (29), when $B \to \infty$, the concentration of the impurity on the surface of a parabolic cylinder is described by the equation

$$C_{\mathrm{f}} = \frac{C_0}{1 - (1 - k)\,(\pi\,\mathrm{Pe})^{1/2} \exp(\mathrm{Pe})\,\mathrm{erfc}\,(\mathrm{Pe}^{1/2})}\,. \tag{48}$$

3.4. Parabolic plate. When $B \to \infty$ and $F = F_0$, Eq. (19) describes a parabolic plate growing in a two-dimensional space. It can be obtained as the section of a parabolic cylinder (see Eq. (45)) by the plane y = const. The radius R of curvature of the top of the parabolic plate is determined by the expression

$$\frac{1}{R'} = \left.\frac{\partial^2 z/\partial x^2}{(1 + (\partial z/\partial x)^2)^{3/2}}\right|_{x=0} = \frac{V}{2DF_0}\,. \tag{49}$$

It follows from Eq. (49) that $F_0 = \mathrm{Pe}' = VR'/2D$, where Pe' is the diffusion Peclet number for the parabolic plate. From Eq. (19) we can find the equation for the shape of the phase interface, $F = F_0 = \mathrm{Pe}'$, in a two-dimensional space. As a result we have

$$z - Vt = \frac{R'(1 - V^2/V_D^2)}{2}\left(1 - \frac{x^2}{(R')^2(1 - V^2/V_D^2)}\right). \tag{50}$$

The distribution of the concentration of the impurity in the liquid near the boundary of the parabolic plate (50) is described as (see (26) and (27))

$$C = (C_{\mathrm{f}} - C_0)\,\frac{\mathrm{erfc}\,((\mathrm{Pe}'u)^{1/2})}{\mathrm{erfc}\,((\mathrm{Pe}')^{1/2})} + C_0\,. \tag{51}$$

The function u in Eq. (51) is found from the expression $\mathrm{Pe}'u = F_+$, where F_+ is the positive root of Eq. (19) when $B \to \infty$. Thus, we can find

$$u = \frac{z - Vt + ((z - Vt)^2 + (1 - V^2/V_D^2)\,x^2)^{1/2}}{R'(1 - V^2/V_D^2)}\,. \tag{52}$$

In accordance with expressions (28) and (29), the concentration of the impurity at the boundary of a parabolic plate is described by the equation

$$C_{\mathrm{f}} = \frac{C_0}{1 - (1 - k)\,(\pi\,\mathrm{Pe}')^{1/2} \exp(\mathrm{Pe}')\,\mathrm{erfc}\,((\mathrm{Pe}')^{1/2})}\,. \tag{53}$$

Conclusions. In the present work, we considered high-speed solidification of a binary system in an isothermal approximation. It is taken into account that the system can solidify with velocities of the order of the diffusion rate in the liquid phase. The model developed involves the finiteness of the diffusion rate and describes the problem of non-Fick diffusion in high-speed solidification of a binary system. This approach to the problem allows one to describe passage to nondiffusion solidification.

A general solution that determines the isoconcentration surface of a crystal that grows with a constant velocity V along a chosen coordinate direction is found based on a locally nonequilibrium description of diffusion mass transfer (see Sec. 2). This solution determines the general case of a stationary distribution of a three-dimensional liquid–crystal interface in the shape of an elliptic paraboloid (see Eq. (19) and Fig. 1a). The found shape of the elliptic paraboloid (19) is a generalization of the classical solution of Ivantsov, Horvay, and Cahn [2-5] to the case of high-speed locally nonequilibrium solidification. In the locally equilibrium limit, when the velocity of diffusion propagation of the impurity is infinite, $V_D \to \infty$, Eq. (19) passes to the classical solution [2-5].

Special forms of growing crystals are found using the general solution (19). In a three-dimensional space, these are a paraboloid of revolution and a parabolic cylinder (see Eqs. (41) and (45) and Fig. 1b and c). In a two-dimensional space, this form is a parabolic plate (see Eq. (50)). All the forms found have an arbitrary configuration that moves along the chosen coordinate direction with a velocity V equal to or higher than the diffusion rate V_D in the liquid volume, i.e., with $V \geq V_D$ (see Subsec. 2.2).

When $V \geq V_D$, passage from convex forms to arbitrary configurations of surfaces, in particular, to a plane front on the scales of diffusion (see [17] and [19]) is accompanied by passage to nondiffusion solidification (i.e., to a phase transformation that is nonseparating in chemical composition). This is expressed in the fact that for $V \geq V_D$ the concentration of the impurity in the liquid volume and on the surface becomes equal to the initial concentration C_0 in the system, i.e., $C(t, x, y, z) = C_0$ and $C_f = C_0$ (see solution (37)). This result has a clear physical meaning [16]: when the velocity V of the interface is equal to or higher than the diffusion rate V_D, a profile of concentration cannot be formed in front of the surface and the system solidifies according to a nondiffusion mechanism. We note that passage to nondiffusion solidification occurs sharply at $V = V_D$ [17, 19]. Here, at $V = V_D$ a bend can be observed on the kinetic curve of velocity–supercooling, and passage from a power law to a linear law of crystal growth occurs [17, 19]. These special features were observed in experiments [10] and theoretical predictions of a model of high-speed dendrite solidification in binary systems [17, 19].

We note that, just like the classical solution [2-5], the solutions (21), (28), (29), (44), (48), and (53) can unambiguously determine only the product of the velocity and the radius of the top, i.e., VR, for a specified value of the concentration. Therefore, to unambiguously determine separate values V and R of the concentration (supercooling or supersaturation in the system), one must use a criterion of selection of the radius of the top. For example, the known criteria of selection in the form of the condition of marginal stability [20], the condition of microscopic solvability [21, 22], and the theory of a surface wave [23] are necessary for their development to the case of locally nonequilibrium mass transfer. The criterion of marginal stability has been used recently to determine a unique radius of the apex of a three-dimensional dendrite rapidly growing in locally nonequilibrium diffusion [17]. This analysis predicts degeneration of the paraboloid into a plane when $V \geq V_D$ and gives satisfactory agreement with experimental data on dendrite growth in binary alloys [17, 19].

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NOTATION

C, concentration of the impurity; $\vec{J}$, vector of the flow of the impurity concentration; D, coefficient of diffusion; $\vec{V}$, vector of the velocity of motion of the phase interface; V, constant velocity of crystal growth along the chosen coordinate axis; C_f and C_s, concentration at the interface on the side of the liquid and solid phase, respectively; k, coefficient of impurity distribution; C_0, concentration at infinity; R, radius of curvature; $\mathrm{Pr} = VR/2D$, Peclet number. Subscripts: n, normal; s, solid; f, front.

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