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The application of the free boundary condition to the problem of binary smelt crystallization

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The problem of impurity diffusion in the melt crystallizing at a constant velocity has been tried to solve by the method of integral functionals with unknown region of integration and free boundary condition. It has been shown that the conditions at the phase boundary are contradictive to each other within the frame of the simplest bidimensional model of solidification. The general problem of existence of a solution for the problem of binary melt solidification is considered.

Осуществлена попытка решения задачи о диффузии примеси в кристаллизующемся с постоянной скоростью расплаве методом интегральных функционалов с неизвестной областью интегрирования и свободным граничным условием. Показано, что в рамках простейшей двумерной модели затвердевания условия на межфазной границе противоречат друг другу. Рассмотрена общая проблема существования решения задачи о затвердевании бинарного расплава.

The numerical methods take an increasing importance in theoretical solving of solidification problems because of essential nonlinearity of these problems [1]. This work is the natural continuation of investigations connected with one of such methods [2]. It has been shown before that for infinitely small bending amplitudes of the boundary between solid and liquid phases in the frame of the simplest bidimensional solidification model of binary melt, its form can be found under consideration of two conditions at this boundary [3]. The approach to the problem of cellular crystal growth developed by authors makes it possible to answer if such conclusion for finite amplitude bending of phase boundary is correct. The aim of this work is to answer this question.

Let the problem be formulated first of all in differential form and then go to its variation equivalent. Let us apply the model of binary melt solidification with semi-infinite diffusion zone [2], combining z axes with crystallization direction. Coordinate z will be measured in D/v units, where D is the impurity diffusion coefficient of in the melt, and v is the crystallization velocity, and count off from the position that crystallization front would occupy if it would be planar. The impurity concentration in the melt $C(z,x)$ will be expressed in $C_0(1-k)/k$ units, starting from the level C_0, where C_0 is the impurity concentration value in the melt at infinite distance from the phase boundary, and k, the impurity distribution coefficient. The phase boundary described by equation $z = \varphi(x)$ will be considered to be periodical in direction x and symmetrical with regard to the period middle. Coordinate x will be measured in semiperiod units l (halfwidth of cells). The diffusion in solid phase and surface energy of phase boundary are supposed to be negligibly small.

Let the following dimensionless coefficients be introduced:

$$\kappa = \frac{D}{vl}, \qquad (1)$$

$$B = \frac{kGD}{(k-1)\mu V C_0}, \quad (2)$$

where G is temperature gradient; μ, the liquidus line slope in the binary system phase diagram.

Then the problem of impurity diffusion in the melt crystallizing at a constant velocity in the region $\varphi(x) \le z < \infty$, $0 \le x \le 1$, can be formulated as:

$$C_{zz} + C_z + \kappa^2 C_{xx} = 0, \quad (3)$$

$$C_z(\varphi) - \kappa^2 \varphi_x C_x(\varphi) + (1 - k)C(\varphi) + k = 0, \quad (4)$$

$$C(\infty, x) = 0, \quad (5)$$

$$C_x(z,0) = C_x(z,1) = 0, \quad (6)$$

$$C(\varphi) = 1 - B\varphi. \quad (7)$$

The coefficients k and B are input parameters here while the coefficient κ is unknown. It is to note also that the condition at phase boundary in the problem (3)–(7) is represented by two equations: (4) and (7), that are boundary conditions of the third and first kind, respectively. Equation (4) is equivalent to condition of impurity balance on crystallization front. Equation (7) follows from the phase diagram, and also from the supposition that temperature field is planar and depends linearly on z [3]. Condition (7) assumes a geometric interpretion [6], that will be used from here on: the concentration values at the phase boundary have to lay in plane (L), defined in the (C, z, x) space by equation

$$C = 1 - Bz. \quad (8)$$

Let the introduce residual functions

$$R(x) = C_z(\varphi) - \kappa^2 \varphi_x C_x(\varphi) + (1 - k)C(\varphi) + k, \quad (9)$$

$$R_1(x) = C(\varphi) - 1 + B\varphi, \quad (10)$$

that characterise the deviations from conditions (4) and (7) along the boundary $\varphi(x)$, and also root mean square residual

$$\sigma = \sqrt{\int_0^1 [R(x)]^2 dx}. \quad (11)$$

Let us now abstract from condition (7) and construct the problem (3–6) solution under fixed phase boundary. Under mathematical physics canons, the solution of such problems exists and is the only one [4]. As it is shown in [2], the minimization of functional

$$IC(z,x),\varphi(x) = \int_0^1 dx \int_\varphi^\infty e^z (C_z^2 + \kappa^2 C_x^2) dz - \int_\varphi e^z [2k + (1 - k)C] C dx, \quad (12)$$

where (φ) means the line $z = \varphi(x)$, along which the curvilinear integral is taken, results simultaneously to equation (3) and condition (4). Thus, the condition (4) can be left free [4], and conditions (5) and (6) can be easily taken into account when selecting the basis functions. The fundamental functions of corresponding boundary problem with planar phase boundary can be used as such ones. Then the solution of problems (3)–(6) can be presented as

$$C_n = \sum_{m=0}^{n} A_{mn} \exp(-q_{mn} z) \cos(m\pi x), \quad (13)$$

where n is the approximation order (0, 1, 2, ...),

$$q_{mn} = 0.5 + \sqrt{0.25 + (m\pi\kappa)^2}, \quad (14)$$

and A_{mn} — coefficients determined basing on the condition of minimum of the functional (12).

Obviously, the consideration of second condition at phase boundary will result in one of two cases: either this condition goes into contradiction with problems (3)–(6) solution and then there is no nontrivial solution of problem (3)–(7), or condition (7) with equations (3)–(6) makes a combined system and their solution can be represented as a pair of functions: $C(z,x)$ and $\varphi(x)$, moreover $\varphi(x) \ne 0$. Here we come to the question, which the work aimed to answer. Let us apply the approach proposed in work [5] to that end.

Let the condition (7) be substituted into the expression (13) to get an equation defining implicit function $\varphi(x)$ in n-th approximation:

$$1 - B\varphi_n = \sum_{m=0}^{n} A_{mn} \exp(-q_{mn}\varphi_n) \cos(m\pi x). \quad (15)$$

Substituting this function into expression (12), we come to integral functional with unknown integrating region. Then the problem (3)–(7) solution is reduced to

searching for functions $C(z,x)$ and $\varphi(x)$, which correspond to conditions (4)–(7) and provide the minimum value of functional (12).

Under stationary state, the impurity concentration at phase boundary has to be on average equal to one, otherwise, the mass conservation law is not met. Then the equality

$$\int_0^1 C(\varphi(x),x)dx = 1. \quad (16)$$

limiting the selection of unkown distributions $C(z,x)$ is valid. Substituting (7) into (16), we get a similar condition for unknown $\varphi(x)$:

$$\int_0^1 \varphi(x)dx = 0. \quad (17)$$

The functional value calculated in n-approximation will be noted as I_n below. As the case when $n = 1$ and $A_{01} = 1$ is of a particular interest, let it be considered separately. Then, in general case, when $A_{01}\neq 1$, the primed symbols will be used (e.g., 1′-th approximation).

The plane problem solution corresponds to zero approximation. To satisfy the condition (4), it is necessary to put $A_{00} = 1$. The unctional (12) becomes equal to $I_0 = -k$. If we add next in (13) component with small amplitude A_{11} to plane solution, we get the solution of the problem with small perturbation [5]. It can be shown that the phase boundary equation in first approximation with respect to A_{11} takes the form:

$$\varphi_1 = \frac{A_{11}}{1-B}\cos\pi x, \quad (18)$$

and functional (11) value to within second infinitesimal order in A_{11} is expressed as

$$I_1 = -k + \frac{A_{11}^2}{4(1-B)^2}[2(1-k)B^2 - 3B + 1 + k]. \quad (19)$$

While in first approximation in A_{11} the condition (17) is fulfilled automatically, the same condition in the second approximation leads to the expression for eigenvalue

$$q_{11} = \frac{1}{2(1-B)}. \quad (20)$$

From the sign of the value $\Delta I_1 = I_1 - I_0$, it can be defined if the planar crystallization front is stable against this perturbation (plus) or not (minus). So for typical value $k = 0.5$, the additive to I_0 in equation (19) is negative at $B<0.634$ and $B>2.37$. Experiment is corresponding (at least qualitatively) to the first of these inequalities. In fact, the stability of planar crystallization front (all other conditions being the same) is breaking only when a certain critical value of crystallization velocity [6] is exceeded, that is, at $v>v_C$, that, according to formula (2), corresponds to $B<B_C$. Then in this example $B_c = 0.634$.

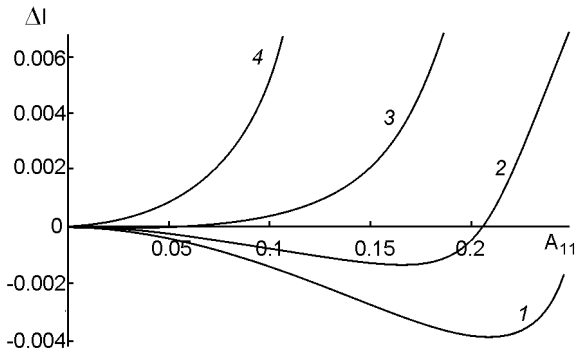

Fig. 1. The dependences of the difference between values of functionals for the 1st- and 0th approximations $\Delta I_1 = I_1 - I_0$ on the perturbation amplitude of A_{11}. Distribution coefficient $k = 0.5$, values of parameter $B = 0.58$, 0.6, 0.634, 0.7 (curves *1*, *2*, *3*, *4*, respectively).

The functional (12) value for finite values of coefficients A are got by numerical method according to the scheme described before [5]. The results given below are got for $k = 0.5$.

Fig. 1 describes the ΔI_1 dependences on the A_{11} amplitude calculated for different values of parameter B. The initial regions of curves in Fig. 1 correspond well to parabolic dependence of I_1 on A_{11} represented by equation (19). The B_c value found in numerical experiment differs by only 0.03 % from that obtained from the same equation. All curves show an end point defined by the collapsing condition of the concentrational over-cooling zone in the center of cellular structure period [5]. The difference from the result obtained before is that the minimum value of functional I1min is attained not at the edge of the solution definition interval but inside it (curves *1* and *2*, Fig. 1).

The results presented below were obtained under parameter value $B = 0.6$, that is, for the case when planar crystallization front is unstable in the criterion $B<B_c$. Minimum of the functional (12) in the first approximation is attained at coefficients values $q_{11} = 1.287$ and $A_{11} = 0.162$. The

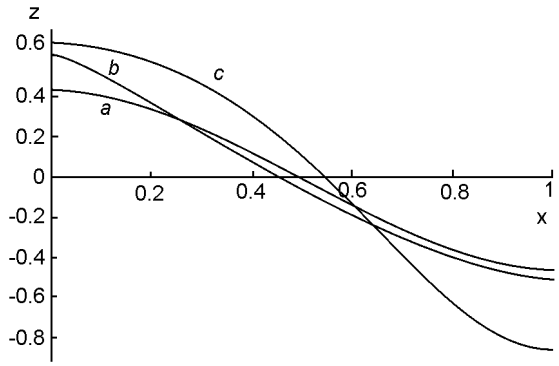

Fig. 2. The phase boundary within the half-period interval under 1st, 1′-th and 2nd approximations (curves a, b and c, respectively) at $k = 0.5$ and $B = 0.6$.

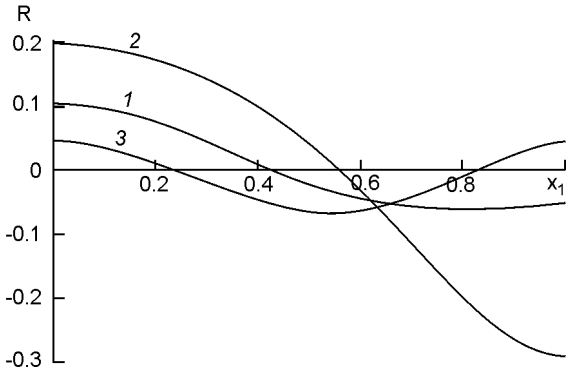

Fig. 3. The dependences of residual R on coordinate x with regard of two conditions at phase boundary under 1st and 2nd approximation (curves *1* and *2*) and at fixed boundary under 2φ-th approximation (curve *3*).

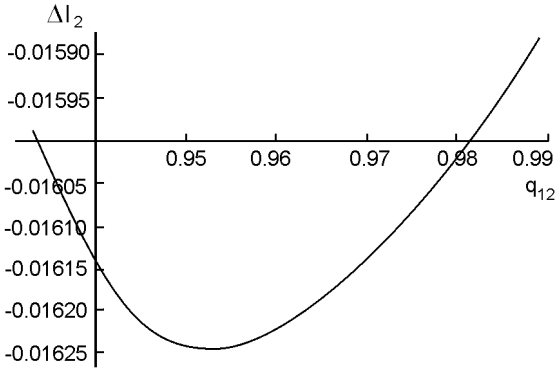

Fig. 4. The dependence of the difference between functional values for the 2nd- and 0th approximations $\Delta I_2 = I_2 - I_0$ on the q_{12} parameter value at $k = 0.5$ and $B = 0.6$.

perturbation amplitude is seen to be rather small, so q_{11} does not differ considerably from the value 1.25 calculated by formula (20) and the phase boundary is close to the line described by the equation (18) (Fig. 2a). Only starting from the 2nd approximation, the phase boundary takes the shape corresponding at least a few to the experiment (Fig. 2c) [6].

Meanwhile, just on the 1st approximation stage, it can be stated definitely that there is no nontrivial solution of problem (3)–(7). In fact, under infinitely small perturbations of planar crystallization front, the plot of function $R(x)$ differs only slightly from zero line $R(x)\equiv 0$. In the 1st approximation for finite perturbations, the amplitude $R(x)$ is significantly different from zero (curve *1*, Fig. 3). As the condition (7) is fulfilled automatically, the increase of amplitude $R(x)$ at transition from infinitely small values to finite ones means that boundary conditions (4) and (7) are contradictory, this contradiction being revealed ever stronger at each further approximation (curve *2*, Fig. 3).

The conclusion about the absence of the solution of problem (3)–(7) at curved boundary is also confirmed by the fact that, starting from 1′-th approximation, the minimum of functional (12) is attained at the values of parameter $q_{1n}<1$ (Fig. 4). According to the formula (14), this is possible only under imaginary value of parameter κ that, taking into account its definition (see formula (1)), has no physical sense. But if we become limited by solution in the region of real values, the minimum of functional (12) is attained at $\kappa = 0$ that is under the cell halfwidth $l = \infty$, that corresponds to trivial solution with planar phase boundary. The calculation made for other values k and B (smaller than B_c) showed that in all cases, starting from a certain n value, the functional (12) takes the least value at $q_{1n}<1$.

The inconsistency of conditions (4) and (7) can be illustrated also by a more traditional way. Let us consider at the problem (3)–(6) with a fixed boundary in the form of line $z = \varphi_1(x)$ obtained under 1st approximation (Fig. 2a). The approximation of n-th order for the case with fixed boundary let be noted as $n\varphi$-approximation. Obviously, for the fixed boundary selected, the 1st- and 1φ-th approximations are coincident to one another, therefore, the residuals $R(x)$ (curve *1* in Fig. 3) coincide, too. The line $z = \varphi_1(x)$ is described by equation (15) (with parameters $n = 1$ and $A_{01} = 1$), so in 1φ-th approximation the boundary conditions of concentration $C(\varphi)$ lay in the plane (L) defined by

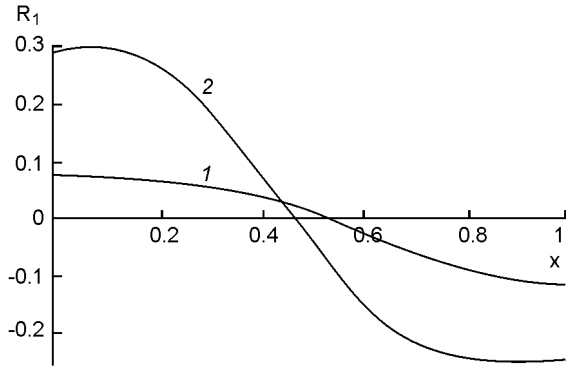

Fig. 5. The dependences of residual R_1 on coordinate x under 2φ-th approximation at fixed phase boundary got under 1st (curve *1*) and 1′-th approximation (curve *2*).

equation (8), and the residual $R_1(x)$ (see formula (9)) coincides with zero line in Fig. 5.

As it was expected, in the case with fixed boundary, the amplitude $R(x)$ is decreased when n increases (curve 3 Fig. 3). But its decreasing is easier judged from decrease of root mean square residual σ (see formula (11)). So, for the curves 1 and 3 (Fig. 3), respectively, we get $\sigma = 0.0598$ and 0.0399. The weak convergence of approximate solution of the problem (3)–(6) to the exact one is an inevitable consequence of application of free boundary condition [4]. Nevertheless, the plot of function $R(x)$ is steady tending to the line $R(x)\equiv 0$ as n increases.

The residual $R_1(x)$ behaves itself quite opposite: at $n>1$, it is not already equal to zero (curve 1 Fig. 5) and while n increases, its plot tends to a curve defined by the pre-specified boundary. The $R_1(x)$ difference from zero means that the boundary conditions of concentration $C(\varphi)$ are not already located within the plane (L), and this is natural, as they are not already connected with plane (L) by correlation (7). If we take the line $z = \varphi_1(x)$ got under the 1′-st approximation as a fixed boundary (Fig. 2b), the increase of the amplitude $R_1(x)$ will be more significant (curve 2 Fig. 5). As the functional I_n values decrease at increasing n both at variable and fixed phase boundary, the increase of amplitude $R(x)$ at the decrease of amplitude $R_1(x)$ and vice versa gives evidence about inconsistency of conditions (4) and (7).

Thus, in the case of finite values, the problem (3)–(7) does not have any solution with non-planar crystallization front. This is explained by the fact that the conditions at phase boundary contradict to each other. Under a closer consideration of these conditions, a direct dependence between their consistency and the used solidification model type is easy to state. Thus, it can be concluded that the simplest bidimentional model used in this investigation is unsuitable for at least a few adequate description of real process of binary melt crystallization. It has been shown also that the solution of the binary melt solidification problem will be primarily defined by the appropriate selection of corresponding model. Therefore, in the problem of binary melt crystallization, not the of phase boundary but the solidification model itself has to be searched for.

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Використання вільної гранічної умови у задачі кристалізації бінарного розплаву

В.М.Каніщев, С.В.Бараннік

Зроблено спробу рішення методом інтегральних функціоналів з невідомою областю інтегрування та вільною гранічною умовою задачі о дифузії домішки у розплаві, що кристалізується з постійною швидкістю. Показано, що у рамках найпростішої двовимірної моделі затвердіння умови на міжфазній границі протиречать одне одному. Розглянуто загальну проблему існування рішення задачі про твердіння бінарного розплаву.