On the variation method in theory of diluted binary melt solidification

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It is shown that the differential problem of bidimentional diffusion of impurity particles in a melt being crystallized at a constant speed could be reduced to variation one by selecting an appropriate integral functional. The use of functional so obtained for stability analysis of the flat crystallization front is exemplified.

Показано, что дифференциальную задачу двумерной диффузии примесных частиц в затвердевающем с постоянной скоростью расплаве можно свести к вариационной, подобрав соответствующий интегральный функционал. Приведен пример применения полученного функционала для анализа устойчивости плоского фронта кристаллизации.

The solid/liquid phase (interphase) boundary is known to acquire cellular structure under some crystallization conditions [1, 2]. In scientific respect, the effect of cell formation in interphase boundary is of not less interest than many other phenomena of self-organization in nonequilibrium systems [3]. But unlike its analog in hydrodynamics, namely, the Bernar's cellular convection, the intent attention of investigators to the above-mentioned effect is dictated first of all by practical needs. It is associated also with the presence of some impurities in real melts as well as intentionally added additives. As cellular growth of crystals is followed by sharp quality deterioration [2], the elucidating of cell formation conditions in the crystallization front is among the primary tasks in the binary melt solidification theory.

In [4], the problem of binary melt solidification was seen from the position of variation principle. The variation problem of impurity diffusion in a melt crystallizing at a constant speed formulated in that work was related to the case of a constant impurity concentration value at the crystallization front or boundary condition of first type. Meanwhile, the condition of impurity balance is to be fulfilled on mobile melt boundary [1], that corresponds to the third type boundary condition. In this case, a functional different from that obtained in [4] will correspond to the differential problem. The purpose of this study is to set the variation problem of impurity diffusion in a melt crystallizing at a constant speed taking into account the third type boundary condition at the crystallization front.

Let us formulate the problem first in differential form and then go to its variation equivalent. Let us use the bidimensional model of binary melt solidification with limited diffusion zone [2], combining the axis z with crystallization direction. Let the coordinate z be measured in D/v units, D being the impurity diffusion coefficient in the melt, and v being the crystallization speed and measured starting from the position that crystallization front would occupy if it would be flat. Let the impurity concentration $C(z,x)$ within the diffusion zone of melt $\varphi(x) \leq z \leq h$ be measured in $C_0(1 - k)[k + (1 - k)e^{-h}]^{-1}$ units starting from the level $C_0 k[k + (1 - k)e^{-h}]^{-1}$, where $z = \varphi(x)$ is the interphase boundary equation, C_0 being the impurity concentration

value that is maintained in the melt at $z \leq h$, and k being the impurity distribution coefficient. Let the interphase boundary be periodic in x direction and symmetric with regard to the middle of period. Let x coordinate be measured in half-period l units (cell half-width). The diffusion in solid phase and surface energy of interphase boundary is supposed to be negligible.

Let dimensionless coefficients be introduced:

$$k = \frac{D}{vl}, \tag{1}$$

$$B = \left(\frac{k}{k-1} - e^{-h}\right)\frac{GD}{mvC_0}, \tag{2}$$

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

Then the impurity diffusion problem in the melt crystallizing at a constant speed in region S pre-defined by inequalities $\varphi(x) \leq z \leq h$, $0 \leq x \leq 1$ can be formulated in the form:

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

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

$$C(h,x) = e^{-h}, \tag{5}$$

$$C_x(z,0) = C_x(z,1) = 0, \tag{6}$$

$$C(\varphi) = 1 - B\varphi. \tag{7}$$

Note that the condition at the interphase boundary is presented by equations (4) and (7) corresponding to boundary condition of third and first types, respectively. Eq. (4) as mentioned before is equivalent to condition of impurity balance at the crystallization front. Eq. (7) follows from the phase diagram and from the assumption that temperature field is flat and depends linearly on z [4].

Now let us abstract from condition (7) and construct the functional to which the solution of the problem (3)-(6) imparts a stationary value. The Eq. (3) could be easily checked to be Euler equation for functional

$$I\{C(z,x)\} = \int_0^1 dx \int_\varphi^h e^z(C_z^2 + \kappa^2 C_x^2)dz. \tag{8}$$

Varying this functional taking into account that the values of impurity concentration at interphase boundary (of pre-specified shape) are not fixed, we obtain

$$\delta I = -2 \int_0^1 dx \int_\varphi^h e^z(C_{zz} + C_z + \kappa^2 C_{xx})\delta C dz - \tag{9}$$
$$- 2\int_{(\varphi)} e^z(C_z - \kappa^2\varphi_x C_x)\delta C dx,$$

where (φ) means the line $z = \varphi(x)$ along which the line integral is taken. Note that the contour of integrating region S, having the line (φ) as a part, is traced in positive direction and that in all regions except (φ), the line integral is equal to zero.

By virtue of stationarity condition and since δC is varied in an arbitrary fashion, the integrands of both integrals in (9) should be equal to zero [5]. The equality to zero of the first one gives the equation (3). But the equality of the second one to zero would mean that the impurity concentration values at interphase boundary are fixed or the first type boundary condition is met. Comparing the integrand of second integral in (9) with third type boundary condition (4), it is easy to write first the variation result from which this condition follows:

$$\delta I = -2 \int_0^1 dx \int_\varphi^h e^z(C_{zz} + C_z + \kappa^2 C_{xx})\delta C dz - \tag{10}$$
$$- 2\int_{(\varphi)} e^z[C_z - \kappa^2\varphi_x C_x + (1-k)C + k]\delta C dx,$$

and then the expression for primary functional (to be sought):

$$I\{C(z,x)\} = \int_0^1 dx \int_\varphi^h e^z(C_z^2 + \kappa^2 C_x^2)dz - \tag{11}$$
$$- \int_{(\varphi)} e^z[2k + (1-k)C]C dx.$$

From the expression for the second variation of functional (11)

$$\delta^2 I = 2 \int_0^1 dx \int_\varphi^h e^z\left(\delta C_z^2 + \kappa^2\delta C_x^2\right)dz - \tag{12}$$
$$- 2\int_{(\varphi)} e^z(1-k)\delta C^2 dx$$

is clear that, at least at $k>1$, the solution of the problem (3)-(6) imparts to this func-

Table. Dependence of impurity concentration C on the distance z to the crystallization front calculated in two approximations and using the accurate formula. $I\{C\}$ is the corresponding value of functional.

	z	0.0	0.2	0.4	0.6	0.8	1.0	$I\{C\}$
$h=1$, $k=0.5$	$C_{I \text{ approx}}$	1.0226	0.8346	0.6751	0.5442	0.4418	0.3679	-0.86524
	$C_{II \text{ approx}}$	1.0009	0.8190	0.6699	0.5484	0.4495	0.3679	-0.86787
	C_{exact}	1.0000	0.8187	0.6703	0.5488	0.4493	0.3667	-0.86788
$h=1$, $k=2$	$C_{I \text{ approx}}$	1.0155	0.8321	0.6756	0.5461	0.4435	0.3679	-2.36590
	$C_{II \text{ approx}}$	1.0008	0.8190	0.6699	0.5485	0.4495	0.3679	-2.36787
	C_{exact}	1.0000	0.8187	0.6703	0.5488	0.4493	0.3667	-2.36787
	z	0.0	0.6	1.2	1.8	2.4	3.0	
$h=3$, $k=0.5$	$C_{I \text{ approx}}$	1.4683	0.8191	0.3527	0.0690	-0.0319	0.0498	0.30057
	$C_{II \text{ approx}}$	1.0659	0.5723	0.2881	0.1491	0.0910	0.0498	-0.53378
	C_{exact}	1.0000	0.5488	0.3012	0.1653	0.0907	0.0498	-0.54979

tional not only stationary value but minimal one. The question if the latter is correct for any k needs a special consideration and is out of this investigation. In this connection, it is of interest to calculate directly the stationary value of the functional

$$I\{C(z)\} = \int_0^h e^z C_z^2 dz - [2kC + (1-k)C^2]_{z=0} , \qquad (13)$$

being the one-dimensional analog of when $\varphi(x) = 0$. For that functional, the accurate solution of the corresponding boundary problem is rather easy to find:

$$C_{exact}(z) = e^{-z}. \qquad (14)$$

Calculations were made by Ritz method for different h and k values. The solution in N-th approximation is presented as a series [5]:

$$C_N = \sum_{n=0}^{N+1} \beta_n z^n, \qquad (15)$$

where β coefficients were found from boundary conditions and the condition of functional stationarity (13). The calculated results for some h and k values are presented in the Table.

The calculation has shown that the approximated solution tends to accurate one and in all cases mentioned ($0 < k \leq 2$ and $1 \leq h \leq 3$), the inequality $I\{C_{\text{exact}}(z)\} < I\{C_N(z)\}$ is observed. These results allow to suppose that the stationary value of functional (11) is equivalent to its minimum in the whole interval of k values. Further (for the simplicity sake) we will not take into account the difference between cases $k < 1$ or $k > 1$,

although in the first case, the existence of function minimizing the functional (11) is only supposed. Thus, the line $z = \varphi(x)$ being preset, the problem (3)-(6) is reduced to minimization of the functional (11) under conditions (5) and (6).

Let us consider an example of the functional (11) application to the stability problem of flat crystallization front of a binary melt. To simplify the problem (3)-(7), let us take the diffusion zone to be half-unlimited ($h \to \infty$). If now we take only small amplitudes of the cell ledges ξ, the solution of this problem in second approximation by ξ can be presented as [6]:

$$C(z,x) = e^{-z} + A_1 \xi \exp(-q_1 z)\cos\pi x + \qquad (16)$$
$$+ \xi^2 [A_0 e^{-z} + A_2 \exp(-q_2 z)\cos 2\pi x],$$

$$\varphi(x) = \xi \cos\pi x + \xi^2 (a_0 + a_2 \cos 2\pi x), \qquad (17)$$

where

$$q_n = 0.5 + \sqrt{0.25 + (n\pi\kappa)^2}. \qquad (18)$$

Let the solution (16), (17) be substituted into each of the conditions at the interphase boundary, decompose the exponents in Teylor's row and assume sums of common factors at $\xi\cos\pi x$, ξ^2 and $\xi^2\cos 2\pi x$ to be equal to zero. Thus, let us make the system of six equations using which we shall get:

$$B = \frac{q_1 - 1}{q_1 + k - 1}, \qquad (19)$$

$$A_1 = 1 - B, \ A_0 = \frac{1}{2}\left(A_1 q_1 - \frac{1}{2}\right),$$

$$A_2 = \frac{A_1(kA_0 + \pi^2\kappa^2 A_{1)} - kA_0}{A_1(q_2 + k - 1) - k}, \qquad (20)$$

$$\alpha_0 = 0, \ \alpha_2 = \frac{A_2 - A_0}{A_1}$$

The solution obtained shows that in the problem (3)-(7), the amplitude of the cell ledges is an independent parameter while the coefficient κ is dependent one, and it can be found from the equation (19) by setting k and B. According to Eqs. (1) and (18), the same equation relates the half-width of cells l with the input parameter B of the problem:

$$l = \frac{\pi D(1 - B)}{v\sqrt{kB[1 - B(1 - k)]}} \qquad (21)$$

As l cannot be negative, the problem can have a non-planar solution only under condition $B\leq1$. This is none other than the condition of concentration overcooling (CO) of the melt [1], that is the base for classical stability criterion of the flat crystallization front, namely, the CO criterion. We get that while the parameter $B>1$, the interphase boundary cannot form cellular structure simply because the condition of impurity balance is not satisfied. It is important, however, that it follows not from the solution of the problem (3)-(7) that at $B<1$, the crystallization front would bend obligatory.

Let us trace now how the value of functional (11) will alter when passing from the flat interphase boundary (ξ = 0) to bent one (ξ ≠ 0). Substituting the expression (16) and (17) into functional (11) and using Eqs. (19) and (20) we get to within second order of smallness in ξ:

$$I = -k + \xi^2\frac{k}{2}\left(B - \frac{1}{2}\right). \qquad (22)$$

It is seen that decrease of the I value due to the interphase boundary bending is possible only under $B<1/2$. Thus, if the CO criterion predicts the formation of growth cells, for example, at crystallization speed values $v>v_1$, then, according to the variation method (VM criterion), this should happen at $v>v_2=2v_1$.

It seems that VM criterion is in contradiction to experimental data, which agree well with equation $B = 1$ correlating the critical values of growth parameters [7]. However, if we present this equation in the generally accepted form:

$$\frac{G}{v} = \frac{(k - 1)m}{kD}C_0 \qquad (23)$$

and change, for example, $2D'$ for D, where D' is "almost the same" diffusion coefficient, then it becomes clear that the proportional dependence between G/v and C_0 values obtained in experiment does not by no means defy the equation $B=1/2$. So the value of the coefficient at C_0 in (23) can be only estimated in most cases.

Thus, taking into account the third type boundary condition, the variation problem equivalent to differential problem of bidimentional impurity diffusion in a melt solidifying at a constant speed has formulated. The application of the functional obtained to problem of flat crystallization front stability results in a critical value of growth speed that is twice higher than crystallization speed at which the concentration overcooling of the melt is observed.

In conclusion, we can note the prospect of the variation approach to the solidification problem. For example, the interphase boundary shape in the problem formulated was preset, while it could be determined by minimizing the functional with indefinite integration region [5]. Although this problem is difficult but it is certainly soluble by means of the same variation methods.

Literature:

1. W. A. Tiller, Crystal Growth from a Melt, in: The Art and Science of Growing Crystals, John Wiley & Sons, Inc., New York - London (1963).
2. B. Chalmers. Principles of Solidification, Wiley, New York, (1964).
3. G. Nicolis, I. Prigogine. Self-Organization in Nonequilibrium Systems.- N.Y.: John Wiley & Sons, 1977.
4. V. N. Kanischev, *Functional Materials*, **8**, 450 (2001).
5. A. D. Myshkis. Mathematics for Technical High Schools: Special Courses, Nauka, Moscow (1974) [in Russian].
6. V. N. Kanischev, *Functional Materials*, **9**, 402 (2002).
7. W. A. Tiller, J. W. Rutter, *Can. J. Phys.*, **34**, 96 (1956).

Про варіаційний метод у теорії затвердіння розбавленого бінарного розплаву

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Показано, що диференційну задачу з двовимірної дифузії домішок у розплаві, що твердіє з постійною швидкістю, можна звести до варіаційної, добравши належний інтегральний функціонал. Наведено приклад застосування отриманого функціоналу для аналізу стійкості плоского фронту кристалізації.