

**On mathematical modelling of growth of an  
individual monocomponent crystal from melt in  
non-uniform temperature field**

by

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A macroscopic mathematical model is proposed for description of the growth of an individual polycrystal immersed into the melt of the same monocomponent substance and placed on an undercooled support. The model approximately describes the spontaneous exit of the boundary layer separating the bulk of the liquid phase from the crystal from its undercooled state, and imitates the crystallographic properties of the crystal by consideration of a fixed lattice whose every cell represents a virtual monocrystal able to adjoin to the existing crystal. For the sake of simplicity the study is restricted to a two-dimensional (planar) framework.

**1. Introduction**

As far as it is known to the author, the mathematical description of the pattern formation in the process of solidification of monocomponent melts or binary alloys in non-uniform temperature fields is so far limited to efforts employing a linear or non-linear stability theory to the Stefan-like problems, formulated for the case of solidification of undercooled melts (Sekerka, 1968; Wollkind and Segel, 1970; Langer, 1980; Wollkind and Notestine, 1981). This approach became the most popular after appearance of the Langer's review (1980) where very impressive results of computations were presented.

In what follows we try to introduce an essentially different model for macroscopic description of the growth of an individual polycrystal, placed on an undercooled support and immersed into the melt of the same substance being in a non-uniform temperature field. Our model is based on rather rough and maximally simplifying assumptions. Therefore it is far from any adequacy to the real physical process. Nevertheless we hope that it may serve as a prototype of a forthcoming model better approaching physical reality.

Our main assumptions are the following:

1. The whole region occupied by the melt and the crystal immersed therein may be imagined as covered by a fixed system of congruent (both geometrically and physically) macroscopic aggregates (cells). These aggregates remain unchanged geometrically and immovable even if the melt moves subject to solidification.

2. The process of solidification/melting consists in the spontaneous, instantaneous transformation of the liquid/solid state of these aggregates into the solid/liquid state. This transformation is accompanied with an instantaneous release/absorption of the relevant latent heat and with a simultaneous increase/decrease of temperature of that aggregate till the thermodynamically equilibrium melting temperature.

3. This process of the change of the phase state takes place only in a boundary layer separating the crystal (melt from the bulk of the liquid) solid phase.

4. The solid phase is considered as an absolutely rigid continuous body whereas the liquid phase as a viscous fluid.

5. The change of the aggregate state is accompanied with the process of a momentary influx of mass into the solid/liquid phase, this flux resulting due the jump of density across the phase interfaces.

6. According to assumptions 4 and 5, the state of the melt is described by Navier-Stokes equations, equation of continuity and by equation of the convective heat transfer subordinated to the classical Fourier law.

7. The thermal state within every aggregate composing the crystal is described by the Fourier equation of heat transfer in a thermally anisotropic continuous body. Conditions of continuity of the temperature and heat fluxes are also valid at the boundaries of different cells within the solid phase of the system as well as at the interfaces crystal-melt.

Since the phase change of any aggregate occurs instantaneously, the process of the change of the phase state in the system is a discrete one.

Solution of the relevant boundary value problem must include determining the sequence of moments when the described instantaneous phase transition takes place in at least one of the aggregates of the system, as well as the evaluation of the temperature within both phases, velocity of motion of the liquid phase, and location of the phase interfaces and their shape. The content of the paper is as follows.

Sec. 2 offers an accurate formulation of all assumptions, Sec. 3-derivation of all governing equations of the problem in a general case and Sec. 4 remarks concerning the relationship between the model proposed and the classical Stefan problem or the Stefan problem with a "negative" latent heat. Several conclusive remarks are formulated in Sec. 5.

## 2. Notations. Geometrical and physical assumptions

In what follows we consider a monocomponent continuous medium filling a given region  $G$  of the Euclidean plane  $R = (X, Y)$  and being in two phase states: solid and liquid. Subregions  $G_{st}$  and  $G_{fl}$  of  $G$  are occupied at the moment  $t$  respectively



by the solid and liquid phase.  $G_{st}$  is supposed to be a connected region whereas  $G_{ft}$  may become disconnected, even if it is connected at the initial moment  $t = 0$ . In the sequel we use notations  $C$  and  $F$  for  $G_{st}$  and  $G_{ft}$ , respectively, understanding by  $C, F$  not only the appropriate subregions of  $G$  but also the material medium filling them.

Assume that  $R$  is covered by an ordered system  $A$  of congruent  $m$ -sided polygons without common points, and such that if  $a$  and  $b$  are two elements of  $A$  and their boundaries have common points then these boundaries coincide along a whole side of the polygons under consideration, or have only one common point — the isolated vertex.

Let  $A^*$  be the subset of cells, entering  $A$ , which is cut from  $A$  by the region  $G$ .  $A^*$  consists of a fixed number of cells, whose part crossecting the boundary  $\partial G$  may not be complete. At every moment  $t > 0$ ,  $A^*$  is divided into two parts  $A_s$  and  $A_f$  cut from  $A^*$  by  $C$  and  $F$ , respectively\*). Let us denote the cells entering  $C$  and  $F$  by letters  $c$  and  $f$  provided with the same subscripts which are assigned to them in the system  $A$ . All cells entering  $C$  are called "crystallits" and those entering  $F$  — "virtual crystallits". The phase transition of a virtual crystallit into a crystallit is designated as  $f_i \rightarrow c_i$ , and the melting of the crystallit — as  $c_i \rightarrow f_i$ , the coincidence of subscripts indicating the geometrical identity of  $c_i$  and  $f_i$  (i.e., they represent the same element of  $A$ ). Notation  $a_i$  is used for any element of  $A$  if its phase state may be not indicated.

Two boundary layers may be associated with  $F$  and  $C$ : the boundary layer  $BF$  consisting of all  $f_i$  such that at least one side of their boundaries belongs to  $\partial C$ , and the boundary layer  $BC$ , consisting of all  $c_i$  with at least one side of their boundaries belonging to  $\partial F$ . Thus  $BF$  separates  $C$  from the bulk of the liquid phase, and  $BC$  — separates  $F$  from the bulk of the crystal  $C$ . Cells  $f_i$  or  $c_i$  having only an isolated vertex on the phase interface  $\bar{F} \cap \bar{C}$  are considered as not belonging to the boundary layer  $BF$  or  $BC$ , respectively.

We use two sets of physical assumptions:

- (a<sub>1</sub>) The liquid phase of the medium under consideration is a homogeneous, isotropic, incompressible fluid of a constant specific heat, density, thermal conductivity and viscosity. Hence Navier-Stokes equations, equation of continuity and Fourier equation of the convective heat transfer must be valid within  $F$ .
- (a<sub>2</sub>) The crystal  $C$  is an absolutely rigid solid of a constant density and specific heat capacity.
- (a<sub>3</sub>) All crystallits  $c_i$  may be considered as macroscopic crystalline aggregates with a constant tensor of thermal conductivity\*\*).

\*)  $C$  and  $F$  consist of the entire cells only, except for those having common points with  $\partial G$ .

\*\*) Periods of crystalline lattices are of order of several Å for simple substances, 10–20 Å for complex organic and inorganic matters of several hundreds Å for crystals of globular proteins and viruses. Taking this into account we may accept as a minimal characteristic size of cells, entering the system  $A$ , the value of several microns. Such a size is great enough for the use the Fourier equation of heat transfer, naturally written for a thermally anisotropic body.

- (a<sub>4</sub>) All crystallits, composing  $C$ , are congruent not only geometrically but with respect to their physical properties, too. This, in particular, means that two different crystallits  $c_i$  and  $c_j$  have the same tensor of thermal conductivity if they are congruently connected with  $c_i$  and  $c_j$ .
- (a<sub>5</sub>) Energy of creation of an unit of length of the interface separating crystallit  $c_i$  from the virtual crystallit  $f_i$  is a constant along every side  $l_{ij}$  of their boundaries, this constant possibly varying with  $j^*$ . Hence the crystallits are anisotropic not only respect to their thermal conductivity but with respect to their surface properties, too.
- (b<sub>1</sub>) The process of the phase transition consists in the spontaneous, instantaneous transform  $f_i \rightarrow c_i$  or  $c_i \rightarrow f_i$  within  $BF$  or respectively within  $BC$ .
- (b<sub>2</sub>) Assuming that the density  $\rho_s$  of the solid phase is greater than  $\rho_f$  — corresponding to the liquid phase, the transform  $f_i \rightarrow c_i$  is accompanied with an instantaneous influx of mass from the bulk of the liquid phase into the cell  $c_i$ . Analogously, the melting  $c_i \rightarrow f_i$  is accompanied with efflux of mass from  $c_i$  into the bulk of the liquid phase. It is assumed that this influx/efflux of mass is uniformly distributed along the whole boundary separating the anew created crystallit/virtual crystallit from the liquid/solid phase.
- (b<sub>3</sub>) The spontaneous, instantaneous phase transition  $f_i \rightarrow c_i$  takes place at the moment  $t_k + 0$  if the following conditions hold at the moment  $t_k - 0$ :
  - (C<sub>1</sub>) Amount of heat to be released in  $c_i$  at the moment  $t_k + 0$  is not less than the amount of heat required for an instantaneous heating  $f_i$  from its temperature at  $t = t_k - 0$  till the melting temperature  $\vartheta_m$ , summed with the amount of heat needed for creating new interfaces to appear as a result of the transform  $f_i \rightarrow c_i$ .  
The analogous situation occurs for the phase transition  $c_i \rightarrow f_i$ .
  - (C<sub>2</sub>) The temperature  $\vartheta_f$  of  $f_i$  subject to the transform  $f_i \rightarrow c_i$  is not greater than the melting temperature  $\vartheta_m$  everywhere in  $f_i$ .  
The analogous situation takes place for the transformation  $c_i \rightarrow f_i$ .
  - (C<sub>3</sub>) Any excess of the heat amount mentioned in  $C_1$  is instantaneously transferred into all cells  $f_j$  and  $c_j$  being in a contact with  $c_i$  and not involved at the moment  $t_k + 0$  into the change of the phase state.  
The analogous situation takes place for the transformation  $c_i \rightarrow f_i$ .

### 3. Governing equations of the problem. The general case

#### 3.1. Description of the system $A$ of crystallits and virtual crystallits

Let  $(x, y)$  be a rectangular Cartesian coordinate system connected with main axes of the ellipse of thermal conductivity of a polygon  $g$ , congruent to all elements  $a_i$  of the system  $A$ , the longer semiaxes being directed along  $x$ -axis. Let  $A^*$  consist

\*) We assume sides of crystallits  $c_i$  enumerated in order of left-hand side circuit.



of  $N$  elements  $a_i$ ,  $i=1, 2, \dots, N$ . Denote by  $(\xi_k, \eta_k)$  the axes parallel to the main axes of thermal conductivity of  $a_k$  and  $(\alpha_k, \beta_k)$  coordinates of the center of the respective ellips in the  $(X, Y)$  coordinate system. We assume that systems  $(x, y)$ ,  $(X, Y)$  and  $(\xi_k, \eta_k)$  have the same scaling.

Let equations

$$x = \alpha_k + a_{k1} \xi_k + a_{k2} \eta_k; \quad y = \beta_k + b_{k1} \xi_k + b_{k2} \eta_k \quad (1)$$

transform  $(\xi_k, \eta_k)$  plane into  $(x, y)$  plane, and equations

$$\xi_k = \alpha_k + a_{k1} x + a_{k2} y; \quad \eta_k = \beta_k + b_{k1} x + b_{k2} y \quad (2)$$

define the inverse transform. Assume also that the transform of the  $(x, y)$  system into  $(X, Y)$  is described by the system

$$X = x_0 + h_1 x + h_2 y; \quad Y = y_0 + g_1 x + g_2 y. \quad (3)$$

Using (1) and (3), one may express  $(\xi_k, \eta_k)$  as functions of  $(X, Y)$ .

Let, further,

$$-l_i x - m_i y + p_i = 0 \quad (l_i^2 + m_i^2 = 1; \quad i = 1, 2, \dots, m) \quad (4)$$

be the normal equation of the  $i$ -th side of the boundary  $\partial g$ . Then, by the congruency of all elements of the system  $A$  the normal equation of the  $i$ -th side of the boundary  $\partial a_k$  in the coordinate system  $(\xi_k, \eta_k)$  is

$$-l_i \xi_k - m_i \eta_k + p_i = 0; \quad i = 1, 2, \dots, m. \quad (5)$$

We may associate with any  $a_k \in A$  its environment consisted of all such elements  $a_{j_k}$ ,  $j_k = 1, 2, \dots, m$  of  $A$  that every side  $l_{ki}$  of  $a_k$  coincides with  $i$ -th side  $l_{j_k i}$  of  $a_{j_k}$ .

Equations (1)–(5) permit to determine common points of  $\partial a_k$  and  $\partial a_{j_k}$  when these elements are described in  $k$ -th and respectively  $j_k$ -th coordinate system.

### 3.2. Equations of heat, mass and momentum transfer

It is convenient to use the  $(X, Y)$  coordinate system for writing equations of heat, mass and momentum transfer in  $F$  at any moment different from those of the instantaneous change of the phase state in the boundary layers  $BF$  and  $BC$ . Denote these moments by

$$0 < t_1 < t_2 < \dots < t_n \dots \quad (6)$$

according to the assumption  $(a_1)$ , equations of momentum, mass and heat transfer in  $F$  are

$$\begin{aligned} d\bar{v}_f/dt + (1/\rho_f) \operatorname{grad} p_f &= \bar{F}_\rho + \nu_f \Delta \bar{v}_f, \\ \operatorname{div} v_f &= 0, \quad \text{for } t \neq t_k \\ \lambda_f \Delta \vartheta_f + Q_f &= c_f \rho_f d\vartheta_f/dt \end{aligned} \quad (7)$$

with the conventional notations used.

Now, let  $c_r$  be any element belonging to  $C$  at the moment  $t \neq t_k$ ,  $k=1, 2, \dots$ . Assuming that there are no sources of heat distributed within the solid phase, we find that in the coordinate system  $(\xi_r, \eta_r)$

$$\lambda^1 \partial^2 \mathcal{G}_s^r / \partial \xi_r^2 + \lambda^2 \partial^2 \mathcal{G}_s^r / \partial \eta_r^2 = c_s \rho_s \partial \mathcal{G}_s^r / \partial t, \quad (\xi_r, \eta_r) \in c_r \quad (8)$$

where

$$\hat{\lambda} = \begin{pmatrix} \lambda^1 & 0 \\ 0 & \lambda^2 \end{pmatrix} \quad (9)$$

is the tensor of thermal conductivity of  $c_r$  in  $(\xi_r, \eta_r)$  — coordinate system and  $\mathcal{G}_s^r$  denotes the temperature of  $c_r$ .

Since  $t \neq t_k$ ,  $k=1, 2, \dots$ , as it is now supposed, continuity conditions for the temperature and fluxes of heat must be satisfied along every common side  $l$  of the boundaries of crystallits  $c_r$  and  $c_j$  or of the crystallit  $c_r$  and the virtual crystallit  $f_j$ . Let

$$q = (\xi_r^0, \eta_r^0) = (\xi_j^0, \eta_j^0) \quad (10)$$

be the point of  $l$  in coordinate systems  $(\xi_r, \eta_r)$  and  $(\xi_j, \eta_j)$ , connected with  $c_r$  and respectively with  $c_j/f_j$ . Denote by  $\mathcal{G}_u^i(\xi_i, \eta_i, t)$  the temperature of  $a_u$  ( $u=s, f$ ;  $i=r, j$ ) at the moment  $t$ . Then, because of the continuity of temperature,

$$\mathcal{G}_s^r(\xi_r^0, \eta_r^0, t) = \mathcal{G}_u^j(\xi_j^0, \eta_j^0, t) \quad (11)$$

where  $u$  is equal to either  $s$  or  $f$  dependently on the nature of the element  $a_u$  under consideration.

Continuity conditions for heat fluxes take the form

$$\lambda^1 \alpha_r \partial \mathcal{G}_s^r(q, t) / \partial \xi_r + \lambda^2 \beta_r \partial \mathcal{G}_s^r(q, t) / \partial \eta_r = \lambda^1 \alpha_j \partial \mathcal{G}_s^j(q, t) / \partial \xi_j + \lambda^2 \beta_j \partial \mathcal{G}_s^j(q, t) / \partial \eta_j \quad (12)$$

or, respectively,

$$\lambda^1 \alpha_r \partial \mathcal{G}_s^r(q, t) / \partial \xi_r + \lambda^2 \beta_r \partial \mathcal{G}_s^r(q, t) / \partial \eta_r = \lambda_f \{ \alpha_j \partial \mathcal{G}_f^j(q, t) / \partial \xi_j + \beta_j \partial \mathcal{G}_f^j(q, t) / \partial \eta_j \} \quad (12^*)$$

Here  $(\alpha_m, \beta_m)$  are direction cosines of the normal to the line  $l$  in the  $m$ -th coordinate system ( $m=r, j$ ).

### 3.3. Conditions satisfied at moments $t_k$ , $k=1, 2, \dots$ , of the spontaneous phase transition

Formulate now conditions which have to be satisfied at moments  $t_k$ ,  $k=1, 2, \dots$  of the spontaneous change of the phase state  $f_i \rightarrow c_i$  (i.e., of the transform of a virtual crystallit into a crystallit). Let  $s$  be the area of  $a_i \in A$ ,  $\gamma$  — be the latent heat of melting per unit of area (i.e., the heat per unit of area to be released at the process  $f_i \rightarrow c_i$  without taking into account the energy of appearance/disappearance of new/existing phase interfaces), and  $\sigma_j$  be the energy of creation of such an interface of unit length along the  $j$ -th side of  $g$ . (We recall that the element  $g$  described in subsection 3.1 is congruent to all aggregates of the system  $A$  of crystallits and virtual crystallits.)

Assume that the thermal state of the system is known at the moment  $t = t_k - 0$ , and that at the moment  $t = t_k + 0$  the transform  $f_r \rightarrow c_r$  takes place. At the moment  $t = t_k - 0$  the boundary  $\partial f_r$  consists of five parts  $S_1, \dots, S_5$  (some of them possibly empty) where

$$\begin{aligned} S_1 &= \partial f_r \cap F \setminus BF \\ S_2 \cup S_3 &= \partial f_r \cap BF \\ S_4 \cup S_5 &= \partial f_r \cap \overline{BC} \end{aligned} \quad (14)$$

so that the new phase interfaces appear at the moment  $t = t_k + 0$  along  $S_1, S_3$  and  $S_5$ , disappear along  $S_4$  and remain unchanged along  $S_2$  (or being more precise: the interfaces liquid-solid are transformed along  $S_2$  into interfaces solid-liquid). We recall that  $BF/BC$  is the boundary layer consisting of virtual crystallits/crystallits separating the crystal/melt from the bulk of the melt/crystal. Then the energy of creation of new phase interfaces at the moment  $t = t_k + 0$  and that of disappearance of existing ones is equal to

$$q' = \sum_{j=1}^m \sigma_j (L_j^1 + L_j^3 + L_j^5 - L_j^4) \quad (15)$$

where  $L_j^i$  is the total length of all  $j$ -th sides of crystallits and virtual crystallits entering  $S_i$ . If  $S_i$  does not contain  $j$ -th sides of crystallits/virtual crystallits, then  $L_j^i = 0$ .

From the other hand the latent heat of the phase transition of the interior of the virtual crystallit  $f_i$  is equal to\*)

$$q'' = \gamma_s + \vartheta_m (c_f - c_s) s \quad (16)$$

We assume that the thermodynamical equilibrium temperature  $\vartheta_m$  is a constant despite the variability of pressure in the system, so that the change of the latter is supposed to be small.

Thus the total energy to be released at the moment  $t = t_k + 0$  is equal to

$$q = q'' - q' = \gamma_s - \sum_{j=1}^m \sigma_j (L_j^1 + L_j^3 + L_j^5 - L_j^4) + \vartheta_m (c_f - c_s) s. \quad (17)$$

Now, let  $\vartheta_f(X, Y, t_k - 0)$  be the temperature of  $f_r$  at the point  $(X, Y)$  in the moment  $t = t_k - 0$ . Then the amount of heat necessary for heating  $f_r$  till the melting temperature is equal to

$$q^* = c_f \rho_f \int_{f_r} (\vartheta_m - \vartheta_f(X, Y, t_k - 0)) dX dY \quad (18)$$

\*) Here  $\gamma$  is the latent heat of an abstract process of solidification which is not accompanied with an isothermal jump of the specific heat capacity after an isothermal transition of the liquid phase into the solid one. Naturally, the second term on the right hand side of (16) may be included into the first one. We recall that  $c_s$  and  $c_f$  are specific heat values per unit of area.



By the condition  $(b_3)$  the moment  $t_k$  is subordinated to the inequalities

$$\begin{aligned} \vartheta_f(X, Y, t_k - 0) &\leq \vartheta_m \quad \forall (X, Y) \in f_r, \\ \vartheta_s(X, Y, t_k + 0) &= \vartheta_m \quad \forall (X, Y) \in c_r, \end{aligned} \quad (19)$$

and

$$q \geq q^*. \quad (20)$$

The excess  $\delta q = q - q^*$  creates an instantaneous flux of heat through the boundary

$$S = S_1 \cup S_3 \cup S_4 \cup S_5 \quad (21)$$

separating  $c_r$  at the moment  $t = t_k + 0$  from that part of its environment having then the temperature at the points of  $S^*$  less or equal to  $\vartheta_m$ .

Let  $\bar{n}$  denote the normal to  $S^*$  outward with respect to  $c_r$  at points of  $S_4$  and  $S_5$ , and inward at points  $S_1$  and  $S_3$ . Then we must have

$$-\lambda_f \vartheta_{fn}|_{S_1 \cup S_3} = (q - q^*) \delta(t - t_k) L^{-1} \eta(\vartheta_m - \vartheta_f)|_{S_1 \cup S_3}, \quad (22)$$

$$(\lambda^1 \vartheta_s^j \alpha_j + \lambda^2 \vartheta_s^j \beta_j)|_{S_4 \cup S_5} = (q - q^*) \delta(t - t_k) L^{-1} \eta(\vartheta_m - \vartheta_s^j)|_{S_4 \cup S_5}, \quad (23)$$

assuming that the crystallite  $c_j$  has boundary side belonging to  $S_4 \cup S_5$  and that the direction cosines are defined in  $j$ -th coordinate system. Here  $L$  is the total length of  $S_1 \cup S_3 \cup S_4 \cup S_5$ ,  $\eta(x)$  is the Heaviside's function and  $\delta(x)$  — the Dirac's delta distribution. (22) and (23) are written with taking into account that, by assumption, the flux of heat created by the non-zero heat excess  $(q - q^*)$  is uniformly distributed along the whole interface accessible to this flux. These conditions are, naturally, valid everywhere along  $S^*$  except for edges where the direction of the normal  $\bar{n}$  is not defined.

We must add conditions determining the mass influx into  $c_r$  being the result of the phase transition  $f_r \rightarrow c_r$ . By the assumption  $(b_2)$ , this instantaneous mass influx is uniformly distributed along  $S_1 \cup S_3 \cup S_5$ . Hence we have

$$\rho_f v_{fn}(X, Y, t) = (\rho_s - \rho_f) (L_1 + L_3 + L_5)^{-1} \delta(t - t_k) \quad (24)$$

for  $(X, Y) \in S_1 \cup S_3 \cup S_5$  and  $t_k \leq t < t_{k+1}$ .

Recalling that the liquid phase is a viscous fluid and that the solid phase is a rigid immobile body, we also find that

$$v_{f\tau}(X, Y, t) = 0 \quad (25)$$

for such  $(X, Y)$  and  $t$ . Here  $v_f$  is the tangential component of  $\bar{v}_f$  on  $\partial c_r$ .

The analogous conditions must be valid if there also occurs the phase transition  $c_r \rightarrow c_f$  at the same moment  $t = t_k + 0$ . In this case instead of  $S_1, \dots, S_5$  we have to consider boundaries

$$\begin{aligned} S_1^* &= \partial c_r \cap (C \setminus BC) \\ S_2^* \cup S_3^* &= \partial c_r \cap BC \\ S_4^* \cup S_5^* &= \partial c_r \cap \overline{BF} \end{aligned} \quad (26)$$



so that again the new phase interfaces appear at the moment  $t = t_k + 0$  along  $S_1^* \cup S_3^* \cup S_5^*$ , disappear along  $S_4^*$  and remain unchanged (in the sense explained above) along  $S_2^*$ . Denoting by  $L_j^i$  the total length of all  $j$ -th sides entering  $S_i^*$ , we obtain instead of (15) \*)

$$q^{*'} = \sum_{j=1}^m \delta_j (L_j^{*1} + L_j^{*3} + L_j^{*5} - L_j^{*4}) \quad (27)$$

whereas (16) remains unchanged. The total energy to be accumulated by  $c_r$  to the moment  $t_k - 0$  is equal to  $q^*$  defined by (17), where  $q''$ ,  $q'$  and  $L_j^i$  must be respectively replaced by  $q^{*''}$ ,  $q^{*'}$  and by  $L_j^{*i}$ . Instead of (18) we now have

$$q^{**} = c_s \rho_s \int_{c_r} (\mathcal{G}_s^r(X, Y, t_k - 0) - \mathcal{G}_m) dX dY \quad (28)$$

Conditions (20), (21) have to be replaced now by

$$\mathcal{G}_s^r(X, Y, t_k - 0) \geq \mathcal{G}_m \quad \forall (X, Y) \in c_r; \quad \mathcal{G}_f(X, Y, t_k + 0) = \mathcal{G}_m \quad \forall (X, Y) \in f_r \quad (29)$$

and

$$q^* \leq q^{**}. \quad (30)$$

Further, instead of (22) and (23) we now have

$$-\lambda_f \mathcal{G}_{fn}|_{S_1^* \cup S_3^*} = (q^* - q^{**}) L^{*-1} \delta(t - t_k) \eta(\mathcal{G}_f - \mathcal{G}_r)|_{S_1^* \cup S_3^*} \quad (31)$$

and respectively

$$(\lambda^1 \mathcal{G}_{s\bar{s}j}^j \alpha_j + \lambda^2 \mathcal{G}_{snj}^j \beta_j)|_{S_2^* \cup S_5^*} = (q^* - q^{**}) L^{*-1} \delta(t - t_k) \eta(\mathcal{G}_r - \mathcal{G}_s^j)|_{S_2^* \cup S_5^*} \quad (32)$$

Finally, instead of (24) and (25), we have

$$-\rho_f v_{fn}(X, Y, t) = (\rho_s - \rho_f)(L_j^{*1} + L_j^{*3} + L_j^{*5} - L_j^{*4}) \delta(t - t_k), \quad (33)$$

$$v_{fr}(X, Y, t) = 0$$

$$\forall (X, Y) \in S_1^* \cup S_3^* \cup S_5^* \text{ and } t_k \leq t < t_{k+1}.$$

Moments  $t_k$ ,  $k=1, 2, \dots$ , are unknown in advance. Therefore computations must be organized as follows.

At  $t=0$  the state of the system is prescribed. Compute, using conditions (7), (8), (10)–(12\*) the distribution of the temperature for  $t>0$  till the moment  $t_1$  such that inequalities (19), (20) or (29), (30) start to be valid for at least one of elements of  $BC \cup BF$ . If this moment  $t_1$  exists the change of the phase state takes place at  $t=t_1+0$ . Use the found state of the system at  $t_1+0$  as a new initial state and continue computations. If, however,  $t_1$  does not exist, i.e., the inequalities (19), (20) or (29), (30) are valid nowhere for all  $t>0$  then the process of the phase transition cannot evolve.

We do not consider here concrete input data. One has only to remember that these data must be chosen so that the growth of an individual crystal may take

\*) Values analogous to  $q$ ,  $q''$  and  $q'$  are now marked by\*.

place, in principle. This means that the temperature less than  $\vartheta_m$  must be prescribed along the support cooling the crystal (this support is a part of the boundary  $\partial G$ ) whereas the rest of  $\partial G$  must be maintained under temperature greater than that of melting, or heat influx into  $G$  must be prescribed along this part of  $\partial G$ . The initial temperature within the crystal must be not greater than  $\vartheta_m$ , and within the melt not less than  $\vartheta_m$ .

Obviously the problem of the crystal generation may also be considered in the case of the region  $C$  degenerated at the moment  $t=0$ , so that at this moment all the system  $A$  consists of virtual crystallites.

#### 4. Relationship between the model proposed and the classical Stefan problem, or the Stefan problem with "negative" latent heat

A natural question arises concerning the possible relationship of our model to the classical Stefan problem and to the Stefan problem for a „supercooled melt” as it is formulated in many papers (See for instance, A. Friedman, 1977; Langer, 1980; Ockendon, 1980), i.e. the Stefan problem with a negative latent heat.

In order to give an heuristic answer to this question consider the simplest case of a thermally isotropic crystal with a rectangular system of crystallites to which corresponds the grid

$$X=ml, \quad Y=nh; \quad m, n = \dots -2, -1, 0, +1, +2, \dots \quad (34)$$

Let us consider a virtual crystallit

$$\{ml < X < (m+1)l; \quad nh < Y < (n+1)h\} \quad (35)$$

subject to the phase change at the moment  $t=t_k+0$ , assuming that

$$f = \{ml < X < (m+1)l; \quad (n+1)h < Y < (n+2)h\} \quad (35a)$$

belongs to the bulk of the liquid phase and the crystallit

$$c = \{ml < X < (m+1)l; \quad (n-1)h < Y < nh\} \quad (36)$$

belongs to  $BC$ . For definiteness consider the case when virtual crystallites entering  $BF$  and contacting  $f$  (see (32)) are not involved into the change of the phase state at the moment  $t_k+0$ , when  $f$  (see (33)) is transforming into  $c$ . Then

$$\begin{aligned} S_1 &= \{ml < X < (m+1)l; \quad Y = (n+1)h\}; \\ S_2 &= \emptyset; \quad S_5 = \emptyset; \\ S_3 &= \{X=ml; \quad nh < Y < (n+1)h\} \cup \{X=(m+1)l; \quad nh < Y < (n+1)h\}; \\ S_4 &= \{ml < X < (m+1)l; \quad Y=nh\}. \end{aligned} \quad (37)$$

Hence

$$L_1 = l; \quad L_2 = 0; \quad L_3 = h; \quad l_4 = l; \quad L_5 = 0; \quad s = lh; \quad L = 2l + h \quad (38)$$

so that

$$q = h(\gamma l - \sigma). \quad (39)$$

Here we assume that the energy of creation of the new interfaces is independent of their location on the boundary of the appropriate crystallit. At the same time

$$\begin{aligned} q^* &= c_f \rho_f \int_{ml}^{(m+1)l} dX \int_{nh}^{(n+1)h} (\vartheta_m - \vartheta_f(X, Y, t_k - 0)) dY \approx \\ &\approx c_f \rho_f (\vartheta_m - \vartheta_f(X^*, Y^*, t_k - 0)) lh \end{aligned} \quad (40)$$

where  $(X^*, Y^*)$  is some internal point of  $f$  under consideration.

Conditions (22), (23) are written assuming that the heat is released instantly at the moment of the spontaneous phase transition. Now, in contrast to this assumption, let us accept the assumption that the heat  $q - q^*$  must be withdrawn from the new created crystallit not instantly, but during the time interval  $(t_k, t_{k+1})$ . Then, instead of (32) and (23), we may write

$$\begin{aligned} \int_{t_k}^{t_{k+1}} dt \int_{ml}^{(m+1)l} (\lambda_s \vartheta_{sy}|_{y=nh} - \lambda_f \vartheta_{fy}|_{y=(n+1)h}) dx = \\ = h(\gamma l - \delta - \rho_f c_f (\vartheta_m - \vartheta_f(X^*, Y^*, t_{k-1})) l) / (l + \frac{1}{2} h) \end{aligned} \quad (41)$$

or, using the mean value theorem,

$$\begin{aligned} \lambda_s \vartheta_{sy}|_{y=nh} - \lambda_f \vartheta_{fy}|_{y=(n+1)h} = \\ = h(t_{k+1} - t_k)^{-1} (\gamma l - \delta - \rho_f c_f (\vartheta_m - \vartheta_f) l) / (l + \frac{1}{2} h). \end{aligned} \quad (42)$$

Let us point out that  $h$  is equal to the displacement of the boundary  $y = nh$  in direction of its normal during the time interval  $(t_k, t_{k+1})$ .

Assume now that  $h \rightarrow 0$ . Then clearly

$$t_{k+1} \rightarrow t_k; \quad \vartheta_f(X^*, Y^*, t_k - 0) \rightarrow \vartheta_m. \quad (43)$$

Hence in the limit we obtain

$$(\gamma - \delta/l) n_t = \lambda_s \vartheta_{sn} - \lambda_f \vartheta_{fn}, \quad (44)$$

i.e., the condition which only differs from the usual Stefan condition by the value of the specific latent heat (per unit area):

$$\gamma - \delta/l > 0 \quad (45)$$

then our condition may be formally considered as a simple discretization of the classical Stefan condition. However, if  $\delta/l > \gamma$  then (44) represents the Stefan condition written for the case of a system with a negative latent heat — the case corresponding to the consideration of the undercooled melt in the above quoted papers.



Another possibility is

$$\begin{aligned} S_2 \text{ or } S_3 &= \{X = ml; \quad nh < Y < (n+1)h\}, \\ S_3 \text{ or } S_2 &= \{X = (m+1)l; \quad nh < Y < (n+1)h\}. \end{aligned} \quad (46)$$

In this case we have, instead of (44)

$$(\gamma - \delta/2l) n_t = \lambda_s \partial_{sn} - \lambda_f \partial_{fn} \quad (47)$$

so that the condition (45) would be replaced by

$$\gamma - \delta/2l > 0. \quad (48)$$

In cases of more complex geometry the effective latent heat may appear to be greater than the volume latent heat  $\gamma$ , less than it or even negative. For example, if  $A$  is composed by hexagons, then the number of appearing and disappearing interfaces may be equal to 5, 4, 3, 2, 1 and respectively 1, 2, 3, 4, 5, so that in two cases the effective latent heat may be greater and in two-smaller than  $\gamma^*$ ). We recall that in the usual Stefan approach the value of surface energy enters into governing equations if and only if the change of the melting temperature due to the change of the principal radii of curvature of the phase interface is taken into account. The growth of the plane interface appears in such an approach as evolving without accumulation of the surface energy.

## 5. Conclusion

As it has been said in introduction we consider the above model as a rough and therefore inadequate one. This inadequacy is, first of all, the result of a macroscopic character of the model, unavoidable when one is studying the influence of external fields on the process of solidification, since the growth of the crystal is really governed by a microscopic level of the process evolution. The growth of the crystal faces is a result of adjoining to it individual particles (atoms/ions) or, with smaller probability, clusters of particles, but not crystallites of a macroscopic size (G. H. Gilmer, 1980).

Dealing with our macroscopic description we were unable to take into account the influence of dislocations and impurities. This is in contrast to digital computer simulations of the growth of an individual crystal using stochastic models (in particular kinetic Ising model) (See, for instance G. H. Gilmer, 1980 and H. Muller-Krumbhar, 1975). These simulations deal with a microscopic level of the process and do not tackle the problem of the influence of non-homogeneity of external temperature field on the dynamics of crystal growth and on its shape.

\*) We assume here that no one of virtual crystallites from the environment of that suffering the phase transition at the moment under consideration is involved into the process of the change of its phase state.

Our model uses arbitrary assumptions concerning the duration of the undercooled state of virtual crystallites. These assumptions are compatible with laws of energy conservation but are not necessary ones. It is known that the metastable undercooled state of a crystal may continue indefinitely long time, whereas in our model the duration of this state is strongly predetermined by the evolution of temperature fields inside the growing crystal and in its environment. This distinction is, perhaps, the most vulnerable place in our model. On the other hand, our model rigorously takes into account the contribution of the change of surface energy into energetic balance of the crystal. This is in contrast to the classical Stefan approach to the problem which is unable to take into account the consumption of energy in the process of enlargement of plane phase interfaces.

Taking all of this into account we can not be so far sure of the sufficient adequacy of our model without any comparison of a representative series of computations with relevant experimental data. Since such comparison has not been performed we consider this paper as being only a preliminary information.

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## O modelowaniu matematycznym wzrostu pojedynczego jednoskładnikowego kryształu z wytopu w niejednostajnym polu temperatury

Zaproponowany zostaje makroskopowy model matematyczny opisujący wzrost pojedynczego polikryształu zanurzonego w wytopie tej samej jednoskładnikowej substancji i umieszczonego na przechłodzonej podporze. Model opisuje w sposób przybliżony spontaniczne wystąpienie warstwy brzegowej rozdzielającej masę fazy płynnej od kryształu znajdującego się w stanie przechłodzonym, odtwarza także właściwości krystalograficzne kryształu dzięki rozważeniu stałej sieci, której każda komórka reprezentuje wirtualny monokryształ mogący przyłączyć się do kryształu istniejącego. Dla uniknięcia dodatkowych komplikacji rozważania ograniczają się do sytuacji dwuwymiarowej (płaskiej).

Предлагается макроскопическая математическая модель описывающая рост отдельного поликристалла погруженного в расплав того же самого материала и расположенного на переохлажденном суппорте.

Чтоб извлечь излишних осложнений все рассуждения ограничены двухмерной постановкой (в плоскости).