Modeling the evolution of a dendritic structure

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The authors give the results of mathematical modeling of the evolution of a dendritic structure with the aid of the model proposed in Ref. 1. They show that, as also in experiment, on the side surface of the model dendrite secondary branches form and develop into the side structure. They make a detailed investigation of its evolution in the process of growth. They show that as time passes the side structure becomes coarser. They study the changes in the dendritic structure in relation to the supercooling. With increasing supercooling the structure becomes denser, then changes to a cellular form, and finally, when the supercooling is greater than one, there is a transition to globular growth forms. A comparison is made with the experimental results.

INTRODUCTION

Recently much interest has been aroused by the problem of structure formation during crystallization. The mathematical difficulties arising in its solution make numerical calculations with computers necessary. Reference 2 reported some results of the application of a model boundary layer in crystallization to the problem of dendritic growth. In Ref. 3 the geometrical model of evolution of the surface of separation of the phases was applied to the same problem.

In Ref. 1 we gave a two-dimensional mathematical model describing the formation and growth of an isolated dendrite in a supercooled one-component melt. The behavior of the system in dimensionless Cartesian coordinates x, z (z being the dendrite growth direction) is represented by the finite-difference equations

$$T_{ij}^{k+1} = (1-4v)T_{ij}^{k} + v[T_{ij+1}^{k} + T_{ij-1}^{k} + T_{i+1j}^{k} + T_{i-1j}^{k}] + \Delta g_{ij}^{k}, \tag{1}$$

$$g_{ij}^{k+1} = g_{ij}^{k} + \Delta g_{ij}^{k}, \tag{2}$$

$$\Delta g_{ij}^{k} = \gamma W_{ij}^{k}(\Delta\theta - T_{ij}^{k}) \tag{3}$$

for a dimensionless temperature T_{ij}^{h} and the fraction of the solid phase g_{ij}^{h} in the cell with number (i, j) at time t_{k}. The parameters v and γ depend on the steps in the temporal and spatial coordinates, while the function W_{ij}^{h} characterizes the capacity of the cell for solidification ($W_{ij}^{h} = 1$ if cell (i, j) at time t_{k} can solidify, otherwise $W_{ij}^{h} = 0$). From (1)–(3) we see that the physical parameter determining the behavior of the system is the relative supercooling $\Delta\theta = C(T_{m}-T_{0})/L$, where T_{0} is the initial temperature, T_{m} is the melting point, and L and C are the latent heat and specific heat of unit volume of the system. At the initial moment a disturbance (x = 0, z = 1) was given on the plane surface of phase separation z = 0 in the form of one solidified cell (x = 0, z = 1) on the axis of symmetry of the system. The physical meaning of Eqs. (1)–(3) in the model is obvious. For its realization we chose a square network. One part is used to calculate the thermal fields of bodies of various shapes. Here the choice of network does not influence the adequacy of the results. However, sequential analysis of the question of the influence of the symmetry of the network on the thermal field and the shape of the growing crystal is difficult.

In Ref. 1 with the aid of this model we analyzed the basic laws of growth of an isolated dendrite at the initial stage. In particular, we showed that an arbitrary perturbation to the plane front in time acquires the form of an acicular crystal, having a tip, stem, and foot by which it is joined to the plane front. We also made a detailed study of the laws of growth of the tip of the needle, which with time acquires a stationary form.

MORPHOLOGY OF DENDRITIC CRYSTAL

Further investigations of the behavior of the above model showed that with time on the side surface of the crystal there appears a periodic system of secondary branches growing in a direction perpendicular to the surface of the main stem (Fig. 1a). This system we shall call the structure of the side branches. The first branch appears at a distance z_{s} from the tip of the dendrite, which can be called the length of the stationary region. Close to the tip, branches are formed at an equal distance d_{s} from one another and are joined to the stem, the thickness $2\delta_{s}$
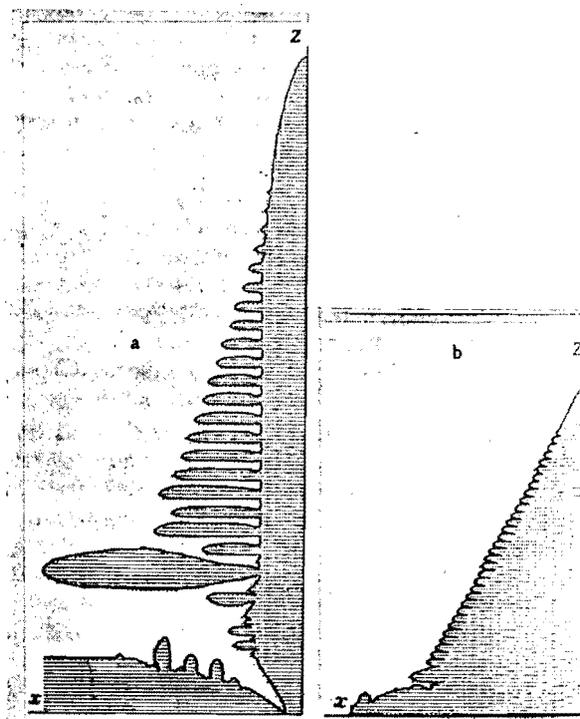

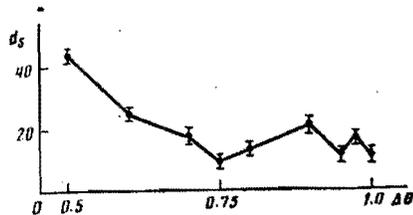FIG. 1. Forms of dendrite at $\Delta\theta = 0.6$ (a) and 1 (b).

FIG. 2. Distance d_s between side branches vs relative supercooling $\Delta\theta$.

of which remains practically constant. The branches slowly become thicker and continuously grow in the lateral direction; with time their rate v_s increases, though it remains less than the rate of growth of the vertex of the main stem v. The side branches have the same morphology as the main crystal, i.e., they consist of a tip, a body, and a foot by which they are attached to the stem of the dendrite, with the difference that the body of the branch is not symmetrical relative to its axis: In the growth direction of the main stem it is more developed than in the opposite one (Fig. 1a). On well-developed secondary branches we observed the appearance of branches of the third order, growing parallel to the main stem.

With increase in the supercooling $\Delta\theta$ from 0.4 to 1 the rate of growth of the side branches v_s increases, i.e., the structure of the side branches becomes more dense (Fig. 2). This is because the thermal length of the field round the growing branch $l_s = 2/v_s$ decreases.

When $\Delta\theta = 1$ the structure of the side branches changes character: Instead of a system of long branches attached to the stem on the side surface of the growing crystal, we get a cellular structure (Fig. 1b). In fact, the whole idea of a stem to the dendrite disappears. Further increase in $\Delta\theta$ to 1.5 and above has the effect that a crystal with a morphologically smooth front begins to grow in the melt (Fig. 3).

This change in the morphology of the crystallization front with increase of supercooling can be called a globular transition. The transition from dendritic to morphologically smooth growth forms at $(T_m - T_0) > L/C$ can be explained by supposing that the latent heat emitted at the crystallization front can be neutralized in a small volume of the melt near it, and thus there is no necessity for branched dendritic growth forms which at lesser supercoolings promote rapid removal of latent heat from the front. Furthermore, with increase in supercooling the thermal length near the vertex of the needle $l_T = 2/v$ decreases and becomes comparable with the radius of curvature of the tip $R = 1/K$, which is the minimal dimension of the structurally nonuniform system (Fig. 5 from Ref. 1).

Change in the form of the dendritic structure with increase in the supercooling has been experimentally observed in the crystallization of supercooled cyclohexanol.[4],[5] In particular, the authors[4],[5] remark that rounded, macroscopically smooth forms appear at a supercooling of about $10°C$. Since for cyclohexanol $L/C = 8.5°C$, therefore the change in the morphology of the crystallization front of this substance occurs at $\Delta\theta \simeq 1.2$, in agreement with the results from the model. The change in intensity of the light scattered from the front in crystallization of supercooled P (Ref. 6) is also attributed by the authors to a change in the morphology of the front from dendritic to
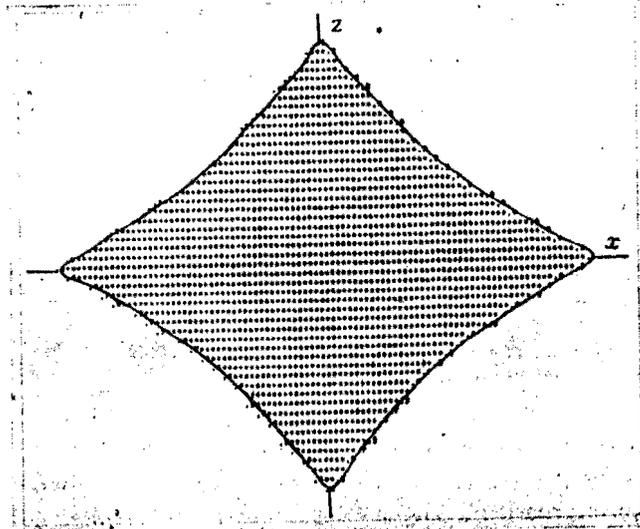

FIG. 3. Form of crystal at $\Delta\theta = 1.5$. Initial seed chosen at center of region.

"quasiplanar." Similar results were given by an investigation of the processes of solidification of metallic ingots based on Fe (Ref. 4) and Ni (Ref. 7). A transition to a morphologically smooth crystallization front with increase in the rate of cooling of metallic alloys was also observed in Ref. 8.

EVOLUTION OF STRUCTURE OF SECONDARY BRANCHES

Interaction of the thermal fields of adjacent branches has the effect that in the structure of the side branches there arises competitive growth, so that this structure becomes coarser. From the model it was found that this phenomenon consists in the fact that each second branch slows down in its development and soon practically ceases to grow (Fig. 1a). The neighboring branches, on the other hand, increase the rate of their growth on account of an increase in the distance between them. The "lost" branch does not remelt (the temperature of its surface in the model did not exceed the phase equilibrium temperature), but in time is taken over by the adjacent branch. This behavior of the structure of the side branches was observed at $0.6 \le \Delta\theta < 1$. At $\Delta\theta \le 0.6$ growth competition apparently appears at later stages than considered in the model.

The behavior of the structure of the side branches can be described by the function $\mathscr{X}(t, z)$, which is the x-coordinate interphase surface at time t at distance z from the vertex of the dendrite. In a system of coordinates linked with the vertex, the evolution of the side structure has the form of a traveling wave arising at some point with increasing amplitude and phase velocity equal to the rate of growth of the tip of the main stem v. With time in the system there is established a state (let us call it asymptotic) such that the crystal is divided into a number of characteristic regions. Throughout the first stationary region the function $\mathscr{X}$ does not depend on time and monotonically increases from zero at $z = 0$ (tip of dendrite) to $\mathscr{X} = \delta$, when $z = z_s$ (boundary of stationary region) (Fig. 4). Regarding z as a parameter, we can state that at this point the stationary behavior of the function $\mathscr{X}(t, z)$ ceases to be stable and at $z > z_s$ it becomes periodic in time with a period $t_s = d_s/v$. In such cases it is said that when $z = z_s$
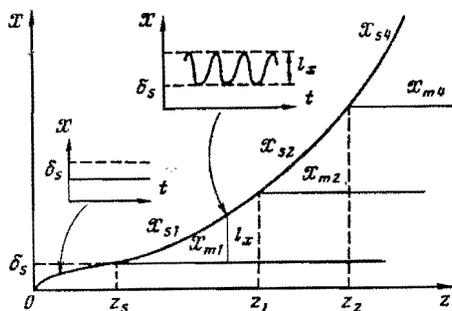
FIG. 4. Scheme of description of evolution of structure of side branches. Insets: behavior of function $x(t)$ at various points z.

there is a bifurcation in the system to a periodic solution (Hopf bifurcation). The envelope $\mathscr{X}_{si}(z)$ of the function $\mathscr{X}(t, z)$ was constructed through the maximal values (tips of branches), and $\mathscr{X}_{mi}(z)$ through the minimal ones (stem of dendrite) (Fig. 1a). As z increases the first function rises rapidly, but the second slowly, which corresponds to the almost constant thickness of the stem $2\delta_S$. Their difference $l_x = \mathscr{X}_{si}(z) - \mathscr{X}_{mi}(z)$ constitutes the length of the side branch at the given point (Fig. 4). $l_x = \mathscr{X}_{sI} - \mathscr{X}_{mI}$

When $z > z_1$ the structure of the side branches becomes coarser. This phenomenon results in the fact that of two adjacent branches one has an increasing growth rate (active branch), and the other a decreasing one (Fig. 1a). Here the spatial period of the structure increases twofold. The function $\mathscr{X}(z)$ is now not repeating in time t_S. This requires two intervals t_S, i.e., the period in time doubles and becomes equal to $2t_S$. In this case we can say that at the point $z = z_1$ in the system there has been a bifurcation with doubling of the period or Feigenbaum bifurcation.[9] Now the function $\mathscr{X}(t, z)$ becomes unstable and moves apart: its ascending branch $\mathscr{X}_{s1}(z)$ corresponds to the tips apices of the active branches, and $\mathscr{X}_{m1}(z)$ to the inactive branches, the length of which is almost constant (Fig. 4).

According to the theory of Feigenbaum, elaboration of the structure occurs by successive bifurcations of doubling of the period. To find the point of the next bifurcation, the was supercooling $\Delta\theta = 0.85$. It was found that after attainment considered of the asymptotic state of the system the structure of the side branches undergoes a second doubling of the period at some point $z = z_2$ (Fig. 5a). On the scheme for the function $\mathscr{X}(z)$ this bifurcation is accompanied by doubling of the branch $\mathscr{X}_{s2}(z)$, from which in turn emerge the growing branch $\mathscr{X}_{s1}(z)$ and the nongrowing branch $\mathscr{X}_{m1}(z)$ (Fig. 4). The full envelope of the dendrite $\mathscr{X}_{s}(z)$, drawn through the vertices of the active branches, is a smooth curve.

A further stage of coarsening of the structure of the side branches was not observed by us owing to the limited possibilities of the computer. Apparently the side structure will also further coarsen by doubling of its period until the growth rate of the active branches becomes equal to the growth rate of the main stem, and on their side surfaces there does not appear a structure of third-order branches analogous to the dendritic structure of the second order arising on the main stem. Thus the evolution of the structure of the side branches is effected by regularly repeating doubling of the distances between the secondary branches.
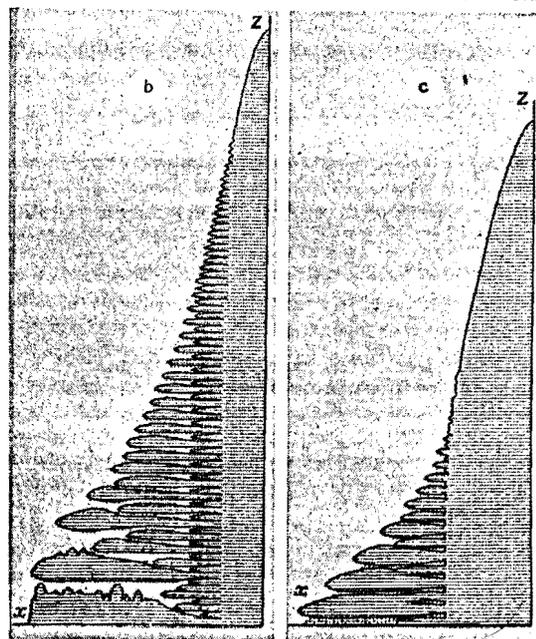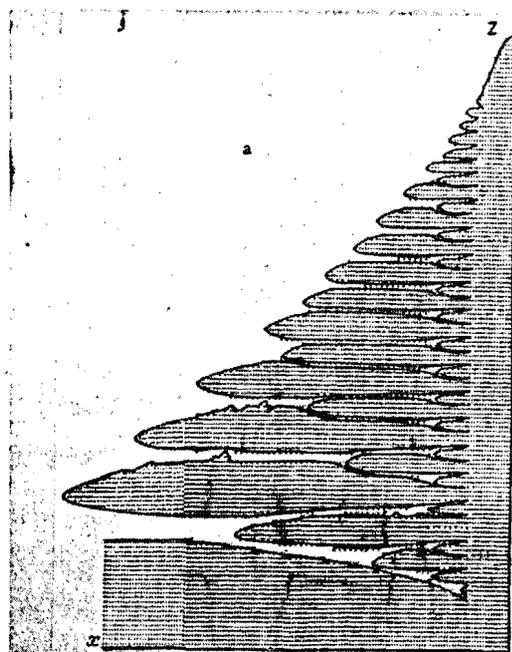

FIG. 5. Forms of dendrites for $\Delta\theta = 0.85$ (a), 0.75 (b), 0.95 (c).

The mechanism of evolution of the structure of the side branches, found in the model, is confirmed by photomicrographs of dendritic crystals of pure substances and alloys. On a photograph of the dendritic structure of the alloy $Sn + 60\% Pb$ (Ref. 10), obtained near the region of maximal diffusion supercooling of the liquid, we see that coarsening of the side structure occurs by doubling of the distance between branches. Figure 3a in Ref. 11 shows a dendrite of NH_4Cl, grown in a supersaturated aqueous solution. Near the tip of the dendrite we can see a close-packed system of equidistant branches. At great distances from the tip the side structure coarsens by doubling of the distances between branches.

The evolution of the side structure of a dendrite of succinonitrile, which is a metal-like organic compound, was studied in Ref. 12. In Fig. 2 of this article we also

see that coarsening of the side structure occurs by doubling of the distance between branches. The authors note that a minute and a half after the formation of the crystal between the active branches there formed a new distance, which exceeded the initial one by a factor of about 15. Apparently here there is coarsening of the structure occurring in the system after four doublings of the distance between branches. Figure 10 in Ref. 12 shows the stage of coarsening of the side structure of the dendrite a long time after its formation. In this case also we see that there is a process of multiple doubling of the distance between branches.

A sign of the action of the above mechanism of evolution of the structure of the side branches is observed in photomicrographs of dendrites of TiS in a melt on an Fe–Ni–Cr base.[13]

In conclusion we note that together with the above laws, we found anomalously rapid change in the side structure in the neighborhood of the points $\Delta\theta = 0.75$ and $\Delta\theta = 0.95$. As we approach the point $\Delta\theta = 0.75$ the side structure comparatively rapidly condenses (Fig. 5b), and the branches grow at equal rates. A dendrite growing with supercooling close to $\Delta\theta = 0.95$ (Fig. 5c) has an anomalously great length of the stationary region, i.e., a practically acicular crystal

grows in the system.

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