tal results of measurements of the refractive indices of NLC will be given in a further article.

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Mathematical model of growth of dendrites in a supercooled melt

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By means of a mathematical model, the authors analyze the formation and growth of dendrites in a supercooled melt. They find how the parameters of dendrite growth depend on the supercooling. They compare the theoretical and experimental results.

INTRODUCTION

As a rule, the growth of crystals from supercooled melts of pure substances is accompanied by the formation of dendrites. Much experimental work has been done on this problem.[1-3] However, owing to the mathematical difficulties, theoretical work has been limited to the description of acicular, unbranched crystals; following Ivantsov,[4] authors usually assume that the tip of the dendrite is parabolic.[5-7] This hypothesis has been verified for slightly supercooled systems.[2,8] However, for relatively great degrees of supercooling it is not justified. The problem thus arises of determining the shape and describing the growth kinetics of dendrites under such degrees of supercooling. This problem can be solved by means of a mathematical model.

Smith[9] has attempted to do this, but obtained no quantitative results. Below we suggest a method and a direct mathematical model of the growth kinetics and shape formation of a dendrite in a supercooled melt of a pure substance.

DESCRIPTION OF MODEL

We shall make a model for the two-dimensional problem. Let us introduce a system of Cartesian coordinates (X, Z). In the region of space $0 \leq x \leq X$, $0 \leq z \leq Z$ with unit length in the third dimension, filled with a supercooled solidifying melt, and for the time variable t > 0, we introduce the difference network $\omega_{x,z,t} = \{x_i = i\Delta x, i = 0,$ $1,\ldots, I;\ z_j = j\Delta z, j = 0, 1,\ldots, J, t_k = k\Delta t, k = 0, 1,\ldots\}$ with steps $\Delta x = X/I$, $\Delta z = Z/J$ in space and Δt in time. The spatial network divides the region into cells with dimension $\Delta x \Delta z$ in the XZ plane. Let the numbers of the cells be those of their top right-hand corners in the network. The state of a cell with number (i, j) at time t_k will be characterized by an average temperature $T_{ij}{}^k$ and a fraction of solid phase $g_{ij}{}^k$ equal to the ratio of the volume of substance crystallizing in the cell to the volume of the cell. For cells filled with solid phase, $g_{ij}{}^k = 1$; for cells filled with melt, $g_{ij}{}^k = 0$; and in solidifying cells, i.e., those which at a given moment contain the phase boundary, $0 < g_{ij}{}^k < 1$.

In time Δt the crystallization process leads to a change in the fraction of solid phase in a solidifying cell by an amount $\Delta g_{ij}{}^k$ and to the separation of an amount $L\Delta x \Delta z \Delta g_{ij}{}^k$ of heat, where L is the latent heat of crystallization of unit volume. The equation of heat balance for such a cell is

$$C\Delta x \Delta z(T_{ij}^{k+1} - T_{ij}^k) = \lambda \Delta t \left[\frac{\Delta z}{\Delta x}(T_{i+1j}^k + T_{i-1j}^k - 2T_{ij}^k) + \frac{\Delta x}{\Delta z}(T_{ij+1}^k + T_{ij-1}^k - 2T_{ij}^k) \right] + L\Delta x \Delta z \Delta g_{ij}^k, \quad (1)$$

where C and λ are the specific heat per unit volume and the thermal conductivity of the medium, which are assumed to be equal for the liquid and solid phases. For the nonsolidifying cells the heat balance obeys the same

equation, but with $\Delta g_{ij}{}^k = 0$. Suppose that part of the boundary, of length $l_{ij}{}^k$, adjoining the (i, j)-th solidifying cell, advances at a rate V_n, measured along the normal to the phase boundary. Then the change in the function $g_{ij}{}^k$ in this cell in time Δt can be represented in the form

$$\Delta g_{ij}{}^k = V_n \frac{\Delta t}{\Delta x \Delta z} l_{ij}{}^k. \tag{2}$$

If the crystal grows by a normal mechanism,[10] then the rate of advance of the front is related as follows to its temperature T_I:

$$V_n = \mu(T_E - T_I), \tag{3}$$

kinetic

where μ is the ~~critical~~ growth coefficient, and T_E is the temperature of equilibrium between the solid and liquid phases, related to the curvature of the phase boundary surface K by the Gibbs–Thompson equation:

$$T_E = T_m\left(1 - \frac{\sigma}{L}K\right), \tag{4}$$

where σ is the surface energy of the phase boundary and T_m is the melting point.

We shall assume that the solid phase can grow only on previously formed solid phase and that nucleation of crystals ahead of the front is not allowed. To realize this condition, in the model we introduce the type of the cell $W_{ij}{}^k$ characterizing the ability of the cell (i, j) to solidify. We put $W_{ij}{}^k = 1$ for solidifying cells ($0 < g_{ij}{}^k < 1$), i.e., for those cells through which the crystallization front passes at a given moment. We also put $W_{ij}{}^k = 1$ for a purely liquid cell ($g_{ij}{}^k = 0$) if it has a common side with at least one completely solidified cell. The remaining purely liquid and purely solid cells are assigned to the type $W_{ij}{}^k = 0$.

Let us introduce dimensionless variables:

$$\frac{C(T_{ij}{}^k - T_0)}{L} \to T_{ij}{}^k, \quad x/\rho_0 \to x, \quad z/\rho_0 \to z, \quad t/\tau_0 \to t,$$

where T_0 is the initial temperature of the supercooled melt, ρ_0 and τ_0 are the characteristic length and time of the problem, related to the characteristic velocity v_0 by the expressions

$$\tau_0 = \alpha/v_0{}^2, \quad \rho_0 = \alpha/v_0, \quad v_0 = \mu L/C,$$

where $\alpha = \lambda/C$ is the thermal diffusivity of the medium. For metals, $\rho_0 \sim 10^{-5}$ cm, $\tau_0 \sim 10^{-9}$ sec, and $v_0 \sim 10^4$ cm/sec.

FIG. 2. Shape of growing dendrite at successive moments of time. 1) Seed at start; 2) acicular crystal; 3) shape of tip, not varying with time; 4) dendrite with side branches.

Suppose $\Delta x = \Delta z$. Then in the new variables, system of equations (1)–(4) can be written in the form

$$T_{ij}{}^{k+1} = (1 - 4\nu)T_{ij}{}^k + \nu[T_{ij+1}{}^k + T_{ij-1}{}^k + T_{i+1j}{}^k + T_{i-1j}{}^k] + \Delta g_{ij}{}^k, \tag{5}$$

$$g_{ij}{}^{k+1} = g_{ij}{}^k + \Delta g_{ij}{}^k, \tag{6}$$

$$\Delta g_{ij}{}^k = \gamma W_{ij}{}^k \xi_{ij}{}^k(\Delta\theta - T_{ij}{}^k - AK_{ij}{}^k), \tag{7}$$

where $\nu = \alpha\Delta t/\Delta x^2$, $\gamma = v_0\Delta t/\Delta x$, $A = \mu\sigma T_m/\alpha L$, $\Delta\theta = C(T_m - T_0)/L$ is the relative supercooling of the melt, and $\xi_{ij}{}^k = l_{ij}{}^k/\Delta x$ is the relative length of the front in the cell; $K_{ij}{}^k$ is the curvature of the interphase surface in cell (i, j), expressed as a multiple of ρ_0^{-1}.

At the starting time, in the supercooled melt a crystal with the same temperature is placed. It occupies the cell with numbers $j = 0$, $i = \overline{1, N}$, and on its planar boundary is placed a disturbance in the form of one solidifying cell in the middle ($g^0_{I/2,1} = 1$). At the boundary cells of the region with $i = 0$, $i = I$, and also $j = 0$, boundary conditions of the second kind are postulated, corresponding to the absence of heat flux and symmetry of the crystal; at the boundary $j = J$ conditions of the first kind are postulated, $T_{ij}{}^k = 0$, corresponding to supercooling of the liquid to a temperature $T_0 < T_m$.

System of equations (5)–(7) with these boundary conditions is a closed system and completely represents the growth kinetics of the new phase and the redistribution of heat in the system.

The results of solution of this problem for various physical systems are similar, with similarity coefficients ρ_0, ν_0, and v_0. The physical parameters which determine the evolution of the system are the relative supercooling $\Delta\theta$ and the coefficient A (7) characterizing the role of the

FIG. 1. Dependence of β on outflow q. Curve: analytical solution from Ref. 11; points: results from model.
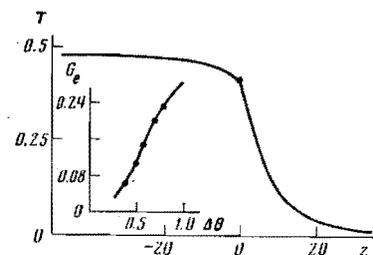
FIG. 3. Temperature distribution along axis of dendrite under supercooling $\Delta\theta = 0.5$. Inset: dependence of G_l on $\Delta\Theta$.
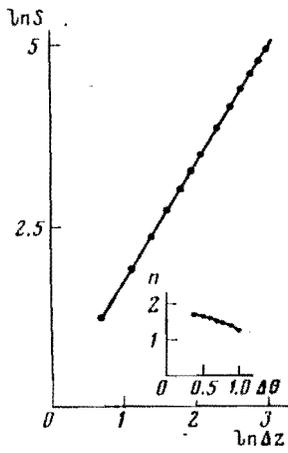
FIG. 4. Logarithm of volume of upper part of dendrite, $\ln S$ vs logarithm of its length, $\ln \Delta z$. Inset: Shape factor n of dendrite vs supercooling $\Delta \Theta$.

surface energy of the boundary in this process, together with ν and γ which are parameters of the numerical scheme.

In the model the initial seed gave rise to a dendrite which grew in the direction of the cooler boundary $z = Z$. As the crystal approached this boundary the whole region was periodically lowered, corresponding to a transition to a system of coordinates associated with the tip of the dendrite. The dimension of the region along the x axis was chosen to be large enough that the influence of the boundaries had practically no effect on the growth of the crystal. In the calculations the function ξ_{ij}^k was replaced by its mean value equal to unity. The growth rate v of the dendrite was determined as the ratio of the length of the cell to the time in which it was traversed by the tip. The curvature of the surface of the dendrite K_{ij}^k at the k-th moment of time in the neighborhood of the cell with number (i, j) was determined as follows. It is known that the curvature of a curve represented by the equation $x = x(z)$ is

$$K(z) = \frac{d^2x/dz^2}{[1+(dx/dz)^2]^{3/2}} = \frac{d}{dz}\left[\frac{dx/dz}{\sqrt{1+(dx/dz)^2}}\right]. \quad (8)$$

The gradient dx/dz of the tangent to the curve bounding the crystal can be found if at the k-th moment of time

FIG. 5. Growth rate v and curvature K of dendrite tip vs supercooling $\Delta \Theta$.
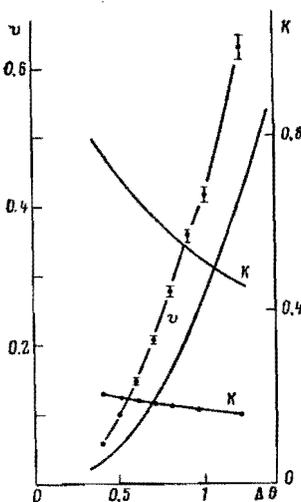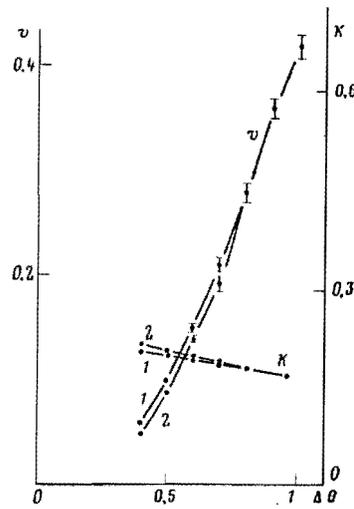
FIG. 6. Influence of surface energy on growth rate and curvature of tip of dendrite. 1) A = 0 or 0.01; 2) 0.1.

we know the field $\{g_{ij}^k\}$:

$$(dx/dz)_j^k = (W_{ij}^k/2) \sum_i (g_{ij+1}^k - g_{ij}^k).$$

At the tip the gradient must be put equal to zero. Then by means of Eq. (8) we can find the curvature of the part of the curve in the neighborhood of the cell (i, j).

A program in FORTRAN-IV was written to solve system (5)-(7) numerically; the algorithm was as follows.

At the initial moment of time $k = 0$ we assigned the initial state of the system. For the change from the k-th to the (k + 1)-th time layer we successively examined all the interior cells of the region (the model showed that the results of the calculations do not depend on the order in which the cells are examined). At first from the field $\{g_{ij}^k\}$ for each cell we determined its type W_{ij}^k. Then from Eq. (7) we found the change of the fraction of the solid phase Δg_{ij}^k, after which from (5) and (6) we determined the temperature T_{ij}^{k+1} and the fraction of solid phase g_{ij}^{k+1} in the cell in the next time layer. At the end of the calculations, in accordance with the boundary conditions we restored the values g_{ij}^{k+1} and T_{ij}^{k+1} in the cells with numbers $i = 0$, $i = I$, $j = 0$, $j = J$. During the calculation we periodically computed the rate of growth of the tip of the dendrite and the curvature of its surface.

In order to choose the optimal values of the parameters ν and γ and for an indirect check on the operation of the proposed algorithm, we used the latter to solve two test problems. In the first we examined the advance of a planar crystallization front in a supercooled liquid. As the second we chose Stefan's problem of solidification with a continuously acting outflow along the axis perpendicular to the plane (X, Z), which at t > 0 removes a quantity q of heat per unit time. This problem has an exact solution[11]: The new phase solidifies in the form of a cylinder at a rate proportional to $t^{-1/2}$. Figure 1 plots the proportionality coefficient β vs the outflow q, obtained in Ref. 11, and also as a result of our model for $\nu = 0.08$ and $\gamma = 0.4$. The discrepancies between the numerical results for both test problems and the corresponding analytical solutions were less than the error
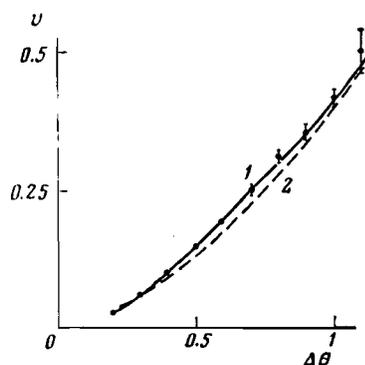
FIG. 7. Dependence of growth rate of acicular dendrites on supercooling $\Delta\theta$. 1) Experimental[1]; 2) theoretical[6]; points, results of model.

in the numerical solutions. In modeling the main problem we chose the same values for ν and γ.

RESULTS FROM MODEL

The model showed that in a supercooled liquid the plane boundary of the phases is unstable, i.e., a slight disturbance to the front (Fig. 2, curve 1) ultimately grows into a needle directed along the Z axis (2), and its shape is independent of the form of the initial disturbance. At some time t_n after the start of the process, a quasistationary state is set up in the system: The tip of the dendrite moves at a constant rate, and a region behind it acquires a constant shape (3). The existence of such a state has been observed in experiments performed directly on transparent organic substances. In the model this result was also obtained for A = 0, i.e., without taking account of the surface energy of the crystal. This proves that the kinetic process of attachment of particles at the phase boundary (3) has a stabilizing action on the growth rate and on the form of the tip of the dendrite. This is because owing to the conditions at the advancing boundary (3) an increase in the velocity of the needle leads to a reduction in the temperature of its surface, and this in turn leads to a reduction in the intensity of the heat flux from the needle. In the later stages of growth the needle is converted to a dendrite with side branches (Figs. 2 and 4). Thus it appears that the shape of the dendrite is stable not only relative to short-wave perturbations of its surface, due to the network character of the solution (the wavelength being of the order of the network dimension), but also relative to long-wave perturbations of the side structure type.

Figure 3 shows a typical temperature distribution along the axis of the dendrite, obtained for the case $\Delta\theta$ = 0.5. The position of the tip of the dendrite corresponds to the point z = 0; for z < 0 we get a crystal in which the temperature is almost uniform; and when z > 0 we get a liquid phase in which there is a large temperature gradient near the tip of the dendrite. The inset to Fig. 3 plots the temperature gradient G_l, averaged over the cell, in the liquid phase at the tip of the dendrite vs the relative supercooling $\Delta\theta$ of the melt.

For numerical analysis the shape of the dendrite surface was determined by the volume S of its upper part, cut off by the plane $z = z_0$, as a function of the distance from this plane to the tip of the dendrite. A typical result for $\Delta\theta$ = 0.5 is shown in Fig. 4. It was found that the surface of the needle, except for a small neighborhood near the tip, can be represented by the equation $x = \varkappa z^{1/n}$ with n < 2. This conflicts with the usual theoretical assumption that the surface of the dendrite is parabolic. The model (inset to Fig. 4) showed that as the supercooling decreases, the index n tends toward two, i.e., the shape of the surface approaches the parabolic.

The points in Fig. 5 show the dependence of the growth rate v and the curvature of the dendrite tip, K, averaged over the cell, on the supercooling, $\Delta\theta$. In this figure the continuous lines correspond to the theory in Ref. 7 with A = 0, in which it was assumed that the dendrite has a parabolic shape. Comparing the results in Fig. 5, we see that parabolic dendrites grow more slowly than dendrites obtained in the model, which have no limitation on the shapes.

For an analysis of the influence of the surface energy on the dendrite growth process we made a model for various values of the surface energy: A = 0 and A = 0.01 (typical metals), curve 1; and A = 0.1 (organic compounds), curves 2 in Fig. 6. The results showed that in the range of supercooling $\Delta\theta \geq 0.4$ the surface energy has practically no influence on the growth rate or the curvature of the tips of metallic dendrites.

We also made a model of the growth of dendrites having the shape of figures of rotation (acicular). Figure 7 shows the dependence of the growth rate of such dendrites on the degree of supercooling. In the range of supercooling $0.2 \leq \Delta\theta \leq 0.5$ this dependence can be approximated by the function $v = 0.48(\Delta\theta)^{1.7}$, in agreement with the experimental results on the growth of dendrites of silver, obtained in Ref. 3, with a kinetic coefficient $\mu = 124$ cm/sec·°C. The solid curve in this figure plots results on the growth of dendrites of phosphorus,[1] with $\mu = 17.7$ cm/sec·K, and the dashed curve plots the theoretical results in Ref. 6.

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