Block-structure aggregation kinetics of a growing crystal

E. A. Brener, M. B. Geilikman, and D. E. Temkin

Solid-State Physics Institute, USSR Academy of Sciences; and I. P. Bardin Scientific and Engineering Institute for Ferrous Metals

(Submitted 19 November 1985)
Zh. Eksp. Teor. Fiz. **90**, 1819–1829 (May 1986)

In this work, we postulate and analyze a mechanism for the block structure aggregation kinetics of a growing crystal, based on the tendency of the crystal to try to reduce the surface energy of its blocks. We find the size distribution function of the blocks and the law describing the growth of the structure off of a planar (on the average) crystallization front for isothermal crystal growth and growth in the presence of a temperature gradient. We present numerical estimates and show that for small block dimensions (smaller than 10^{-2}–10^{-3} cm) the growth law is linear with time, while for larger dimensions the growth law is logarithmic. We also show that for a macroscopically convex front (i.e., convex to the melt side) the crystallization growth of the structure proceeds faster (an exponential law) than for a planar front.

The problem of structural ("pattern") selection in crystal growth is characteristic of a whole series of nonequilibrium systems. In addition to such well-known examples as Rayleigh-Benard thermoconvection, this problem has recently been intensively studied in relation to the growth of dendrites[1,2] and snowflakes,[3] as well as eutectic[4,5] and porous[6,7] crystallization. These nonlinear systems, despite their many differences, have a common feature: at a certain critical value of some specific control parameter, the original homogeneous state becomes unstable. In the present instance, the control parameter has to do with the supercooling of an originally liquid phase, or with a temperature gradient (for a fixed rate of crystallization). The question which arises concerns the time evolution of the inhomogeneous state, and finally the selection of that structure which is actually realized.

The evolution of the structure of an inhomogeneous state was studied early in the development of the theory of phase transitions, primarily with regard to the kinetics of coalescence of nucleation units[8] during the decay of a supersaturated solution. Then, in the work of I. M. Lifshitz,[9] the growth kinetics of domains with different orientations of the order parameter was discussed for second-order phase transitions.

In the present work, we investigate the analogous question of growth of a domain structure; however, in contrast to Ref. 9, we will deal with processes related to first-order phase transitions. In this case, there is a transition front between the initial and final phases, whose motion determines the kinetics of these processes. We will investigate the kinetics of formation of a domain structure in the final phase, taking into account only the kinetic processes at the transition front, assuming that inter-domain boundaries within the volume of the final phase are frozen in place. Obviously, this question has a rather general character; however, for definiteness we will have in mind the growth of crystals from a melt. A domain structure can arise, first of all, during the growth of an ordered crystal in which domains can exist with differing orientations of the order parameter. In addition, domains can be single-crystal regions, i.e., grains, mis-oriented relative to one another as a result of dislocation formation and the amalgamation of the latter into small-angle boundaries. In all these cases, the interdomain boundaries possess a supplementary surface energy, so that in time growth of the domain structure must occur. This mechanism leads to the following qualitative behavior: since domain boundaries or blocks have surface energy, in order for equilibrium to hold at a triple point we must require local warping of the crystallization front (see Fig. 1). The local supercooling at the front will depend on the block dimensions; the orientation of the block boundaries relative to the direction of crystal growth will also turn out to be different for blocks of differing sizes. For this reason, the block sizes change as time passes: blocks whose size exceed a certain average value grow larger, while blocks smaller than this average size shrink. These latter blocks ultimately "collapse"; hence, the characteristic size scale of the structure grows with time.

In the following sections of this work, we analyze in

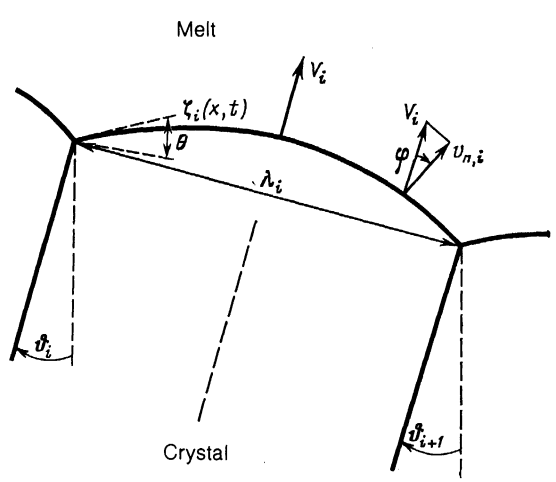

FIG. 1.

 0038-5646/86/051067-06$04.00

detail the process of domain (block) structural growth in the presence of a temperature gradient. We find the size distribution function for the blocks and the time dependence of the growth of the structure.

We note that the geometric selection of a domain structure has been investigated before,[10] along with the growth mechanism connected with macroscopic shifting of the transition front into the melt region.[11] The role of this mechanism will be discussed in the last section of this paper.

ISOTHERMAL GROWTH

Let us investigate the isothermal growth of a crystal from a thin sample melt. Near the crystallization front, the crystal has a certain block structure (see Fig. 1). The motion of the crystallization front $\zeta_i(x,t)$ can be described by the equation:

$$v_n = v_0(1+R_c k), \tag{1}$$

where

$$v_n = \frac{\partial \zeta_i}{\partial t}\Big/\left[1+\left(\frac{\partial \zeta_i}{\partial x}\right)^2\right]^{1/2}, \quad k = \frac{\partial}{\partial x}\left[\frac{\partial \zeta_i/\partial x}{[1+(\partial \zeta_i/\partial x)^2]^{1/2}}\right] \tag{2}$$

are the normal velocity of growth and curvature of the front; v_0 and R_c are the rate of growth of a plane surface and the radius of a critical-sized nucleus for the supercooling ΔT in question. Equation (1) must be supplemented by boundary conditions at the juncture of three lines, i.e., a "triple junction". First of all, the condition of continuity of the crystal front must hold:

$$y_i = \zeta_i(x_i(t),\ t) = \zeta_{i-1}(x_i(t),\ t). \tag{3}$$

Second, if the mobility of the triple point is large enough, thermodynamic equilibrium must hold at this point, i.e., the angle between the line tangent to the front and the line perpendicular to the block boundary at this point must be fixed. Neglecting the anisotropy of the surface energy, we will assume this angle is constant at all triple junctions. Then the equilibrium condition at a triple junction can be written in the form

$$\begin{aligned} \partial \zeta_i/\partial x &= \operatorname{tg}(\theta-\vartheta_i), \\ \partial \zeta_{i-1}/\partial x &= -\operatorname{tg}(\theta+\vartheta_i), \end{aligned} \tag{4}$$

where ϑ_i is the angle between the growth direction and the tangent to the block boundary at the ith triple junction. The angle ϑ_i is connected with the velocity components $\dot{x}_i$ and $\dot{y}_i$ of the triple point by the obvious relation

$$\operatorname{tg}\vartheta_i = \dot{x}_i/\dot{y}_i. \tag{5}$$

Equations (1)–(5), together with initial conditions, completely describe the growth kinetics of the block structure. The formulation of this problem for the entire volume is very complex, and in what follows we will investigate only the quasi-static approximation. By this approximation we mean the following: for a fixed block size λ_i the front is described by stationary equations, i.e., it moves without change of shape with a certain velocity V_i normal to λ_i (see Fig. 1). In order for this approximation to make sense, the characteristic time it takes to establish the stationary front must be appreciably shorter than the time for the value of λ_i to change.

The correctness of the quasistatic approximation and the behavior of the system for $\lambda \ll R$ can be understood qualitatively from the following considerations: for a given set of block sizes λ_i, over a large section of the front $1 \gg \lambda$ a stationary configuration is established, which moves with constant velocity V. Then the ith block, moving with velocity $v_n = V$ according to (1) must have a front curvature k_i which does not depend on the index i, that is

$$k \sim (2\theta+\vartheta_{i+1}-\vartheta_i)/\lambda_i = 2\theta/\lambda_0,$$

where λ_0 is a characteristic size scale of the structure. The rate of change of the size of a block can be estimated thus:

$$\dot{\lambda} = v_0(\vartheta_{i+1}-\vartheta_i) \sim v_0\theta[\lambda/\lambda_0 - 1].$$

The characteristic time for a block dimension to change can be estimated from this relation to be $\tau_\lambda \sim \lambda_0/v_0\theta$. After this time, according to (1), the stationary motion of the crystallization front is established aong the line

$$l \sim (v_0 R_c \tau_\lambda)^{1/2} \sim \lambda_0 (R_c/\lambda_0\theta)^{1/2} \gg \lambda_0,$$

that is, as we assumed, over a distance significantly larger than λ_0. Thus, the rate of change of the block dimensions depends on the ratio (λ/λ_0). Those blocks with dimensions smaller than λ_0 continue to shrink and eventually collapse. Because of these processes, the number of blocks in the system decreases while the characteristic scale of the structure increases. Thus, the question which arises is analogous to that of coalescence of domains dealt with in Ref. 8.

Best on these qualitative considerations, we now undertake systematic calculations using the quasistatic approximation. In this approximation, the equation of motion takes the form

$$V_i \cos\varphi = v_0(1 - R_c d\varphi/ds), \tag{6}$$

where the curvature $k = -d\varphi/ds$, φ is the angle between V_i and v_n, and s is the arc length measured from the ith triple point. In the quasistatic approximation, the form of the front $\zeta_i(x,t)$ is symmetric relative to a line perpendicular to the middle of λ_i; the angle φ in the vicinity of the triple junction satisfies the relation

$$-\varphi(0) = \varphi(s_i) = \theta + (\vartheta_{i+1}-\vartheta_i)/2.$$

As a result of integrating equation (6) for these boundary conditions, we obtain the following equation for the velocity V_i:

$$\frac{V_i}{v_0} = \frac{4R_c v_0}{\lambda_i[v_0^2 - V_i^2]^{1/2}} \operatorname{arctg}\left[\left(\frac{v_0+V_i}{v_0-V_i}\right)^{1/2} \operatorname{tg}\left(\frac{\theta}{2} + \frac{\vartheta_{i+1}-\vartheta_i}{4}\right)\right] - \frac{R_c}{\lambda_i}[2\theta + (\vartheta_{i+1}-\vartheta_i)]. \tag{7}$$

For small angles $\theta \ll 1$ and $(\vartheta_{i+1} - \vartheta_i) \ll 1$, and λ_i not too large,

$$\lambda_i\theta/R_c \ll 1, \tag{8}$$

from (7) we have

$$V_i=v_0[1-2R_c\theta/\lambda_i-R_c(\vartheta_{i+1}-\vartheta_i)/\lambda_i], \tag{9}$$

and in the limit of large λ_i ($\lambda_i\theta/R_c\gg 1$)

$$V_i=v_0[1-2(\pi R_c/\lambda_i)^2]. \tag{10}$$

In the quasistatic approximation, the coordinates x and y of the triple junction are related to the block dimensions by the following expressions:

$$\begin{aligned} x_{i+1}-x_i&=\lambda_i\cos[(\vartheta_i+\vartheta_{i+1})/2],\\ y_{i+1}-y_i&=-\lambda_i\sin[(\vartheta_i+\vartheta_{i+1})/2]. \end{aligned} \tag{11}$$

Taking the time derivative of the relation

$$\lambda_i=[(x_{i+1}-x_i)^2+(y_{i+1}-y_i)^2]^{1/2} \tag{12}$$

and using (11) and (5), we obtain

$$d\lambda_i/dt=\sin[(\vartheta_{i+1}-\vartheta_i)/2]\,[\dot y_i/\cos\vartheta_i+\dot y_{i+1}/\cos\vartheta_{i+1}]. \tag{13}$$

The velocity of the ith triple junction along a tangent to the block boundary $\dot y_i/\cos\vartheta_i$ is connected with the normal velocities of the fronts $v_{n,i-1}$ and $v_{n,i}$ on both sides of it by the obvious relation

$$v_{n,i-1}=v_{n,i}=(\dot y_i/\cos\vartheta_i)\cos\theta. \tag{14}$$

Within the quasistatic approximation under investigation here, the normal velocity for motion of the front at the triple junction is connected to the velocity V_i by the following relation

$$v_{n,i}=V_i\cos(\theta+(\vartheta_{i+1}-\vartheta_i)/2). \tag{15}$$

Then from (14) and (15) we obtain the result that within this approximation the quantity

$$\begin{aligned} \frac{\dot y_i}{\cos\vartheta_i}&=V_i\frac{\cos[\theta+(\vartheta_{i+1}-\vartheta_i)/2]}{\cos\theta}\\ &=V_{i-1}\frac{\cos[\theta+(\vartheta_i-\vartheta_{i-1})/2]}{\cos\theta}=V=\text{const} \end{aligned} \tag{16}$$

does not depend on the index i, and consequently is constant along the front.

As a result, we obtain from (13) and (16) the following system of equations for determining the change in the width of a block

$$d\lambda_i/dt=2V\sin(\Delta\vartheta_i/2), \tag{17}$$

$$V=V_i(\lambda_i,\,\Delta\vartheta_i)\,[\cos(\Delta\vartheta_i/2)-\sin(\Delta\vartheta_i/2)\operatorname{tg}\theta], \tag{18}$$

where $\Delta\vartheta_i=\vartheta_{i+1}-\vartheta_i$.

Since the velocity V_i determined in the general case by equation (7) will depend on λ_i and $\Delta\vartheta_i$, equation (18) couples $\Delta\vartheta_i$ with the quantity λ_i.

GROWTH OF THE STRUCTURE WITH TIME

Let us investigate the change in the size scale of the structure with time in the limit of large values of λ when $\lambda\theta/R_c\gg 1$. In this case V_i is determined by expression (10). Let us introduce a characteristic length scale of the structure λ_0 connected with its characteristic growth velocity V by the following relation:

$$V=v_0[1-2(\pi R_c/\lambda_0)^2]. \tag{19}$$

Eliminating $\Delta\vartheta_i$ from equations (17) to (19) and taking into account the smallness of the parameter $R_c/\lambda\theta$ we obtain for the rate of change of the block dimension the equation

$$\dot\lambda_i=\frac{(2\pi R_c)^2v_0}{\lambda_0^2\operatorname{tg}\theta}\left[1-\left(\frac{\lambda_0}{\lambda_i}\right)^2\right]. \tag{20}$$

It is clear from (20) that blocks with dimensions larger than λ_0 tend to grow while blocks smaller than λ_0 tend to shrink. Eventually these latter blocks "collapse". Thus, this mechanism causes the number of blocks in the system to decrease, and the characteristic scale λ_0 of the structure grows with time, analogous to the coalescence problem investigated in Ref. 8.

Let us introduce into our discussion a time-dependent distribution function $f(\lambda,t)$ for the block sizes, in such a way that $f(\lambda,t)\,d\lambda$ is the number of blocks per unit length along the front whose size lies in the interval λ to $\lambda+d\lambda$. This distribution function satisfies the continuity equation

$$\frac{\partial f}{\partial t}+\frac{\partial}{\partial\lambda}(f\dot\lambda)=0, \tag{21}$$

where $\dot\lambda$ is determined from formula (20). The function f is normalized by the condition

$$\int_0^\infty \lambda f(\lambda,t)\,d\lambda=1. \tag{22}$$

The continuity equation (21) was written down for a distribution function f which is homogeneous along a planar front. (In the presence of a macroscopically curved front, $\mathscr{H}$ in equation (21) should have in addition a term $\partial(f\dot s)/\partial s$, where s is the coordinate along an arc of the "macro-front", while

$$\dot s=\int_0^s V_n\mathscr{H}\,ds$$

is the rate of change of the coordinates of blocks whose boundaries are expanding perpendicular to the "macro-front" and moving with normal velocity V_n).

In order to determine the distribution function $f(\lambda,t)$ and the function $\lambda_0(t)$ asymptotically at large times, we seek a self-similar solution to equations (21), (22) in the form

$$f(\lambda,\,t)=A\lambda_0^{-2}(t)\varphi(u), \tag{23}$$

where $u=\lambda/\lambda_0(t)$, A is constant which is determined by the normalization condition (22). Substituting (23) into (21), we find the asymptotic variation of $\lambda_0(t)$ with time and an equation for the function $\varphi(u)$:

$$\lambda_0(t)=[(2\pi R_c)^2v_0t/\gamma\operatorname{tg}\theta]^{1/3}, \tag{24}$$

$$u\frac{d\varphi}{du}[u^3-3\gamma(u^2-1)]=2\varphi(3\gamma-u^3), \tag{25}$$

where the self-similarity parameter γ takes on a specific value in the limit of large times. Analogous to the coalescence problem,[8] the constraint that the distribution function be normalizable for this value of γ gives rise to a cutoff point u_0 for the system (i.e., for $u\geqslant u_0$, $\varphi(u)=0$). The coordinate of the cutoff point u_0 and the value of the self-similar parameter

γ are determined by the condition that the function in the square brackets in equation (25) reduce to zero along with its derivative, i.e.,

$$u_0=\sqrt{3}, \quad \gamma=\sqrt{3}/2. \tag{26}$$

Integrating equation (25) for this value of γ, we find the self-similar distribution function

$$\varphi(u)=\frac{u^2\exp[-2/(3-\sqrt{3}u)]}{(u+\sqrt{3}/2)^{10/9}(\sqrt{3}-u)^{26/9}}. \tag{27}$$

Let us now find the link between the parameter λ_0 introduced above and the average characteristics of the structure. Multiplying equation (21) by λ, integrating it over $d\lambda$ and using (22), we find

$$\lambda_0^2=\int f(\lambda)\,d\lambda \Big/ \int \lambda^{-2}f(\lambda)\,d\lambda, \text{ т. е. } \langle\lambda^{-2}\rangle=\lambda_0^{-2}. \tag{28}$$

Taking this circumstance into account, equation (10) gives

$$\langle V_i\rangle=V.$$

For small values of the angle θ, in the problem we are studying here there is an intermediate asymptotic regime in which the characteristic structure scale satisfies

$$\lambda_0 \ll R_c/\theta.$$

The velocity V_i introduced in equation (18) is determined by relation (9); let us introduce the characteristic length scale λ_0 of the structure, connected with the characteristic growth velocity V:

$$V=v_0(1-2R_c\theta/\lambda_0). \tag{29}$$

Eliminating $\Delta\vartheta_i$ from equations (17), (18) and (29), and taking into account the smallness of the parameter $\lambda_0\theta/R_c$, we obtain the following equation for the rate of change of the block size:

$$\dot{\lambda}_i=2v_0\theta[\lambda_i/\lambda_0-1]. \tag{30}$$

Solving equations (21)–(23) in this case, we obtain

$$\lambda_0(t)=2\theta v_0 t/\gamma, \tag{31}$$

$$\varphi(u)=\begin{cases}\exp(-u) & \text{at } \gamma=1,\\ [u+\gamma/(1-\gamma)]^{(\gamma-2)/(\gamma-1)} & \text{at } 0<\gamma<1.\end{cases} \tag{32}$$

If in the beginning the size distribution function for large blocks is exponentially small, then the self-similarity parameter $\gamma=1$. In the case when the initial distribution has an integrable power-law "tail" with exponent δ, according to (32) the value of γ is given by $(\gamma-2)/(\gamma-1)=\delta$. The average value of the structure parameter $\langle\lambda\rangle$ over this distribution coincides with λ_0, while the averaging of the growth velocity gives $\langle V_i\rangle=V$. The self-similar function (31), describing the intermediate asymptotic behavior, goes over to the asymptotic function (24) for values of the structure parameter $\lambda_0\sim R_c/\theta$ and times $t\sim R_c/v_0\theta^2$.

CRYSTALLIZATION IN A TEMPERATURE GRADIENT

Let us investigate the analogous problem of the growth of a crystal by block structure aggregation in the case where the furnace is "dragged" along the system with velocity v_0 with a constant temperature gradient G. Since the dragging velocity v_0 is given, the problem reduces to finding the position of the crystallization front in the furnace (for example, relative to the location where the temperature equals the melt temperature as determined by the equilibrium phase diagram). In the course of time, the block structure will grow, and corresponding to this growth the position of the crystallization front changes.

Let us first investigate the steady-state growth of an ordered structure with block dimension λ_0. The position of the crystallization front $\zeta(x)$ is described by an equation relating the normal growth velocity to the local supercooling

$$v_n=v_0\cos\varphi=\beta[-G\zeta+\Gamma k], \tag{33}$$

where φ is the angle between the direction of velocity v_0 and the normal to the front, β is the kinetic growth coefficient, and Γ is a constant proportional to the boundary energy separating the phases. At the triple juncture, the value $|\varphi|=\theta$. For small angles, $\varphi\sim\zeta'$, and equation (33) can be cast in the form

$$\frac{d\varphi^2}{d\zeta}+\frac{\varphi^2}{R_c}-\frac{2}{L_G^2}(\zeta+L_G^2/R_c)=0. \tag{34}$$

Here, we introduce the notation $R_c=\beta\Gamma/v_0$ for the radius of a critical nucleus for a kinetic supercooling rate v_0/β, and $L_G=(\Gamma/G)^{1/2}$ for the capillary length. Integrating equation (34), we obtain

$$\varphi^2/2=\frac{R_c^2}{L_G^2}\left(\frac{\zeta-\zeta_m}{R_c}\right)+\left(\frac{R_c^2}{L_G^2}\frac{\zeta_m}{R_c}+1-\frac{R_c^2}{L_G^2}\right)\times\left[1-\exp\left(\frac{\zeta_m-\zeta}{R_c}\right)\right], \tag{35a}$$

$$x=-\frac{R_c}{\sqrt{2}}\int_0^{(\zeta-\zeta_m)/R_c} dy\left\{y\left(\frac{R_c}{L_G}\right)^2+(1-\exp(-y))\times\left[1+\left(\frac{R_c}{L_G}\right)^2\left(\frac{\zeta_m}{R_c}-1\right)\right]\right\}^{-1/2}, \tag{35b}$$

where ζ_m is the front position for $\varphi=0, x=0$. We denote by ζ_0 the front position at the triple-juncture level ($|\varphi|=\theta$, $x=\lambda_0/2$). Solving equation (35), we find the value of $|\zeta_m|$ and $|\zeta_0-\zeta_m|$ for various limiting cases:

a) $\lambda_0\ll R_c/\theta$, $\lambda_0\ll L_G$:

$$|\zeta_m|=(L_G^2/R_c)(1+2\theta R_c/\lambda_0);$$

$$\times\ |\zeta_0-\zeta_m|=\lambda_0\theta/4\ll|\zeta_m|; \tag{36a}$$

b) $R_c/\theta\ll\lambda_0\ll L_G$:

$$|\zeta_m|=(L_G^2/R_c)[1+2(\pi R_c/\lambda_0)^2];$$

$$\times\ |\zeta_0-\zeta_m|=2R_c\ln(\lambda_0\theta/2\pi R_c)\ll|\zeta_m|; \tag{36b}$$

c) $R_c/\theta\ll L_G\ll\lambda_0$:

$$|\zeta_m|=(L_G^2/R_c)[1+(R_c/L_G)^2\exp(-\lambda_0/2L_G)]; \tag{36c}$$

$$|\zeta_0-\zeta_m|=2R_c\ln(L_G\theta/R_c\sqrt{2})\ll|\zeta_m|;$$

d) $L_G \ll \lambda_0$, $L_G \ll R_c/\theta$:

$$|\zeta_m| = (L_G^2/R_c)\,[1+(4R_c\theta/L_G)\exp(-\lambda_0/2L_G)]; \tag{36d}$$

$$|\zeta_0 - \zeta_m| = L_G\theta.$$

In cases (a) and (b), the change in temperature over the length scale of the structure is small, i.e., the distorted front is in fact isothermal. Therefore, the analysis presented in the previous sections is entirely correct here, and the change as a function of time in the scale $\lambda_0(t)$ of the structure is given by formulae (31) in case (a) and (24) in case (b). However, for crystallization in a temperature gradient, as λ_0 increases not only the growth velocity but also the position of the crystallization front ζ_m changes, corresponding to expressions (36a) and (36b).

In the second pair of cases (c) and (d), for $\lambda_0 \gg L_G$ the influence of the temperature variation on the scale of the structure is appreciable. The position of the crystallization front and the supercooling at that point depend exponentially on λ_0. Thus, one can expect that the growth of the structure takes place much more slowly than in the previous cases.

For definiteness let us investigate the situation where $R_c/\theta \gg L_G$ for the growth of the block structure. In equation (34) we can therefore neglect terms in φ''/R_c. Then solving equation (34) with the boundary conditions (4), we find for the ordinates of the triple junctions that

$$y_i = L_G\left\{\frac{2(\theta+\vartheta_{i+1})+(\theta-\vartheta_i)\,[\exp(\lambda_i/L_G)+\exp(-\lambda_i/L_G)]}{\exp(-\lambda_i/L_G)-\exp(\lambda_i/L_G)} - \frac{L_G}{R_c}\right\}, \tag{37}$$

$$y_{i+1} = L_G\left\{\frac{2(\theta-\vartheta_i)+(\theta+\vartheta_{i+1})\,[\exp(\lambda_i/L_G)+\exp(-\lambda_i/L_G)]}{\exp(-\lambda_i/L_G)-\exp(\lambda_i/L_G)} - \frac{L_G}{R_c}\right\}.$$

For $\lambda_i \ll L_G$, we have from (37) that

$$y_{i+1} = y_i = -L_G^2\{[2\theta+(\vartheta_{i+1}-\vartheta_i)]/\lambda_i + 1/R_c\}, \tag{38}$$

i.e., y_i does not depend on the index i, and is constant along the front. In this case, as we have already noted, we return to the equation of motion (30) and the function $\lambda_0(t)$ determined by relation (31).

For $\lambda \gg L_G$, from equation (37) and the continuity condition for the front (3), we find

$$\dot{\lambda}_i = v_0(\vartheta_{i+1}-\vartheta_i)$$
$$= v_0\theta[\exp(-\lambda_{i+1}/L_G) - 2\exp(-\lambda_i/L_G) + \exp(-\lambda_{i-1}/L_G)]. \tag{39}$$

Unlike all the previous cases, the rate of variation $\dot{\lambda}_i$ of the block size given by (39) varies not only with the local value λ_i but also with the sizes of the neighboring blocks. A similar nonlocal equation of motion was investigated by Langer[4] as a model for analyzing structure selection in the growth of eutectics.

To find the growth law of the block structure with time, in place of the exact nonlocal equation (39) we will investigate this equation in the mean-field approximation, i.e., we replace the quantities $\exp(-\lambda_{i+1}/L_G)$ and $\exp(-\lambda_{i-1}/L_G)$ by their average values, which we denote by

$$\langle \exp(-\lambda/L_G)\rangle = \exp(-\lambda_0/L_G).$$

Let us introduce the dimensionless variables $\tau = 2v_0\theta t/L_G$, $\tilde{\lambda} = \lambda/L_G$. The distribution function f satisfies the continuity equation (21):

$$\frac{\partial f}{\partial \tau} + \frac{\partial}{\partial \tilde{\lambda}}\{f[\exp(-\tilde{\lambda}_0) - \exp(-\tilde{\lambda})]\} = 0 \tag{40}$$

and the normalization condition (22).

In the region $\tilde{\lambda} > \tilde{\lambda}_0$ in (40), we can neglect the term $e^{-\tilde{\lambda}}$ compared to $e^{-\tilde{\lambda}_0}$ (recall that $\tilde{\lambda}_0 \gg 1$). Thus, the general solution to equation (40) takes the form

$$f(\tilde{\lambda}, \tau) = \psi\left(\tilde{\lambda} - \int \exp[-\tilde{\lambda}_0(\tau)]\,d\tau\right), \quad \tilde{\lambda} > \tilde{\lambda}_0, \tag{41}$$

where the function ψ determines uniquely the form of the initial distribution function in the large $\tilde{\lambda}$ region.

In the region $\tilde{\lambda} < \tilde{\lambda}_0$, neglecting $e^{-\tilde{\lambda}_0}$ compared to $e^{-\tilde{\lambda}}$ we find

$$f(\tilde{\lambda}, \tau) = \exp(\tilde{\lambda})\,g[\tau + \exp(\tilde{\lambda})], \quad \tilde{\lambda} < \tilde{\lambda}_0, \tag{42}$$

where g is an arbitrary function. We determine this function from the "connection" formulae (40) and (41) for $\tilde{\lambda} = \tilde{\lambda}_0$, and thereby obtain an approximate solution.

It is clear from the normalization condition (22) that the distribution function in the large-$\tilde{\lambda}$ region must fall off rather quickly: either as an exponential or as a power-law $\tilde{\lambda}^{-\delta}$, $\delta > 2$. We can show that in both of these cases the condition of the time-independence of the integral (22) leads to the conclusion that for asymptotically large times τ, to leading order the argument of the function ψ in (41) should not depend on time for $\tilde{\lambda} = \tilde{\lambda}_0$. This condition yields the dependence

$$\tilde{\lambda}_0(\tau) = \ln \tau. \tag{43}$$

In fact, in the case of exponential decay of the distribution function in the large-$\tilde{\lambda}$ region, $\psi(x) \sim e^{-\alpha x}$. From the "connection" formulae (41) and (42), for $\tilde{\lambda} = \tilde{\lambda}_0$ we find

$$g(\tau)\exp(\tilde{\lambda}_0) = \exp\{-\alpha[\tilde{\lambda}_0 - \textstyle\int \exp(-\tilde{\lambda}_0)\,d\tau]\},$$

and for the normalization integral we obtain

$$\int_0^\infty \tilde{\lambda} f(\tilde{\lambda}, \tau)\,d\tilde{\lambda} \sim \tilde{\lambda}_0(\tau)\exp\left\{-\alpha\left[\tilde{\lambda}_0 - \int \exp(-\tilde{\lambda}_0)\,d\tau\right]\right\}. \tag{44}$$

The dependence (43) implies an exponent in (44) which is time-independent. In the next approximation, in order to reduce the time dependence of the coefficient of the exponential it is necessary to assume that

$$\tilde{\lambda}_0 - \int \exp(-\tilde{\lambda}_0)\,d\tau \approx \frac{1}{\alpha}\ln\ln\tau \ll \ln\tau, \tag{45}$$

i.e., $\tilde{\lambda}_0 \approx \ln\tau + (\alpha\ln\tau)^{-1}$.

For the case of a power-law decay of the distribution function in the large-λ regime, we have $\psi(x) \sim x^{-\delta}$ ($\delta > 2$),

and in place of (45) we obtain

$$\tilde{\lambda}_0 - \int \exp(-\tilde{\lambda}_0)\, d\tau \approx (\ln \tau)^{1/(\delta-1)} \ll \ln \tau.$$

Thus, for $\lambda_0 \gg L_G$ and asymptotically large times the scale of the structure grows at a logarithmically slow rate according to

$$\lambda_0(t) = L_G \ln (2v_0\theta t/L_G). \tag{46}$$

DISCUSSION

In this work we have used the quasistatic approximation to analyze the growth of a block structure. This approximation leads to the condition that the velocity of a triple junction V is constant along the front. The time it takes this regime to be established along a length of front l is estimated to be

$$\tau_l \sim l^2/v_0 R_c.$$

This estimate is derived from a diffusion problem with diffusion coefficient $v_0 R_c$, as a characteristic time over which a solution is nonsteady; this diffusion problem in turn is a consequence of equation (1). Along with the time τ_l, there is a characteristic time τ_λ over which the block dimension changes. This time can in various limiting cases be determined by linearizing equations (20) and (30)

$$\tau_\lambda \sim \frac{1}{8\pi^2}\frac{\lambda_0^3\theta}{v_0 R_c^2} \quad \text{at} \quad \lambda_0 \gg R_c/\theta,$$

$$\tau_\lambda \sim \lambda_0/v_0\theta \quad \text{at} \quad \lambda \ll R_c/\theta.$$

The quasistatic approximation is applicable for those parts of the front of this length l which contain a large number of blocks, i.e., $l \gg \lambda_0$, while at the same time τ_l remains smaller than τ_λ. From estimates of τ_l and τ_λ it follows that

$$l < \lambda_0(\lambda_0\theta/8\pi^2 R_c)^{1/2} \gg \lambda_0 \quad \text{at} \quad \lambda_0 \gg R_c/\theta,$$

$$l < \lambda_0(R_c/\lambda_0\theta)^{1/2} \gg \lambda_0 \quad \text{at} \quad \lambda_0 \ll R_c/\theta.$$

From this it is clear that the conditions for the quasistatic approximation to apply will be fulfilled. Depending on the increase of the structure size scale λ_0, these conditions hold over all portions of the crystallization front larger than λ_0.

In conclusion, we present some numerical estimates. Let us take the following values as characteristic for the system parameters: $\beta \sim 10$ cm s^{-1} K^{-1}, $\Gamma \sim 10$ K $-$ cm, $\theta \sim 10^{-1}$ and the adjustable growth parameters $v_0 \sim 10^{-3}$ cm/s^{-1}, $G \sim 10^2$ °cm^{-1}. Then the characteristic value of the length R is 1 cm, while $L_G \sim 10^{-3}$ cm. So long as the characteristic length scale of the structure satisfies $\lambda_0 < L_G$, the growth of the blocks is described by the dependence (31), i.e., $\lambda_0 \sim v_0\theta t$. After a time $t \sim L_G/v_0\theta \sim 10$ s the average block size reaches a value L_G (at which point the crystal has grown to a size $L \sim v_0 t \sim 10^{-2}$ cm); after this, the time dependence of the structure's growth changes over to logarithmic, i.e., (46). Thus, for a crystal which has grown to the size $L \sim 10^2$ cm, the characteristic block dimension amounts to $\lambda_0 \sim L_G \ln(L\theta/L_G) \sim 10 L_G \sim 10^{-2}$ cm.

The macroscopic shift of the crystallization front into the melt region (which can be controlled by selecting the corresponding thermal conditions) can substantially accelerate the process of block growth. Actually, the presence of a macroscopically curved front introduces an additional contribution $\lambda \mathcal{K} v_0$ to the rate of change of the block dimension $\dot{\lambda}$. According to (39), for logarithmic growth $\dot{\lambda} \sim v_0\theta \exp(-\lambda/L_G)$. Thus, for $\lambda\mathcal{K} \gtrsim \theta \exp(-\lambda/L_G)$, i.e., for

$$\lambda \gtrsim L_G \ln(\theta/L_G\mathcal{K})$$

the growth of the structure will take place not logarithmically but exponentially:

$$\lambda_0 \sim L_G \ln(\theta/L_G\mathcal{K}) \exp(v_0\mathcal{K}t). \tag{47}$$

The length of a fully-grown crystal, i.e., one at which we make the transition to the dependence (47) is $L \sim \mathcal{K}^{-1}$.

Let us assume that the curvature is on the order of the transverse dimension of the crystal, i.e., $\mathcal{K} \sim 10^{-1}$ cm^{-1}. Then the block structure in fact disappears for $\lambda_0\mathcal{K} \sim 1$. From (47) we find that this occurs when the crystal has grown to a length

$$L \sim \mathcal{K}^{-1} \ln(1/L_G\mathcal{K}) \sim 10^2 \text{ cm}.$$

The mechanism for growth of the structure which we have investigated here ultimately must lead to the disappearance of all the blocks. However, we observe in experiments that a certain finite density of blocks remain. This can be related to our neglect of block nucleation processes, and also to the presence of special low-energy boundaries which expand along the growth axis.

[1] J. S. Langer, Rev. Mod. Phys. **52**, 1 (1980).
[2] E. Ben-Jacob, N. Goldenfeld, B. G. Kotliar, and J. S. Langer, Phys. Rev. Lett. **54**, 2110 (1984).
[3] E. Ben-Jacob, N. Goldenfeld, J. S. Langer, and G. Schon, G. Phys. Rev. A **29**, 330 (1984).
[4] V. Datye, R. Mathur, and J. S. Langer, J. Statist. Phys. **29**, 1 (1982).
[5] J. S. Kirkaldy, Phys. Rev. B **30**, 6889 (1984).
[6] G. Dee and R. Mathur, Phys. Rev. B **27**, 7073 (1983).
[7] M. Kerszberg, Phys. Rev. B **28**, 247 (1983).
[8] I. M. Lifshits and V. V. Slezov, Zh. Eksp. Teor. Fiz. **35**, 479 (1958) [Sov. Phys. JETP **8**, 331 (1958)].
[9] I. M. Lifshits, Zh. Eksp. Teor. Fiz. **42**, 1354 (1962) [Sov. Phys. JETP **15**, 939 (1962)].
[10] A. N. Kolmogorov, Dokl. Akad. Nauk SSSR **65**, 681 (1949).
[11] C. Elbaum, Progr. Metal. Phys. **b**, 203 (1959).

Translated by F. J. Crowne