# Instability and formation of regular structures during cooling of gas-saturated liquids and solids

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The simple nonlinear equation $a = \Delta a^2$, describing "parquet" patterns on a front which result in the "pencil structure" of growing crystals, has been obtained for the well-known "Stefan problem" of the motion of the solidification front of a supercooled liquid, when instability of the Mullins-Sekerka type develops. A new, "bulk" mechanism of filamentation and self-organization of nonlinear flows of heat and gas, flowing out of the cooling solid body, is studied. This mechanism could lead to the "columnar structures" which are observed in nature and also have a structure of the stack-of-hexahedral-pencils type.

## 1. INTRODUCTION

When crystals are grown from melt there sometimes arise structures that look like a stack of tightly packed hexahedral pencils whose ends form a "parquet" structure. This well-known phenomenon is caused by the instability of the solidification front (SF) of the melt.

The problem of the motion of the solidification front is known in the literature as "Stefan's problem."[1] The solidification front becomes unstable when the liquid ahead of it is in a supercooled state with temperature $T$ less than the solidification temperature $T_3$. This instability is customarily called the Mullins-Sekerka instability for a flat SF.[2] Together with the temperature, impurities can also play a significant role in this process. The diffusion of impurities is described by the same equations as the equation for the temperature. These mechanisms also explain the formation of the complicated structure of snowflakes and other "dendritic" crystals.[3]

These phenomena are reviewed in, for example, Ref. 4, where a quite complicated integrodifferential equation $z = z_f = a(t, x, y)$ describing the SF is presented and solved by numerical methods.

In the first part of the present paper we briefly recount the results of Ref. 4 pertaining to the case of only a flat SF, and we show that in the steady state the surface of the SF can be determined approximately from a much simpler nonlinear equation $a = \Delta a^2$. In the one-dimensional case it gives approximately the profile of the surface of the SF in the form $a(x) \propto [1 - \cos(kx)]^{1/3}$, which is in good agreement with the experiments of Jackson[5] and in the two-dimensional case describes on the SF a parquet pattern of hexagons which engender the "pencil structure" of the crystals.

Part 2 of the present paper examines the superficially similar problem of the appearance in nature of hard pencil structures, termed in volcanology "columnar structures" and "stacks," encountered in volcanogenic regions. Thus in the USSR extensive areas with "parquet" and rocks consisting of tightly packed hexahedral blocks (see Fig. 1) are found on Mys Stolbchatyi on Kunashir Island in the Kuril Islands. There arises the question: how do they form from the cooling volcanic magma?

In the volcanological literature (see, for example, Ref. 6) the most common opinion is that they are formed as a result of settling of the rock, resulting in fragmentation of the rock along a honeycomb system of cracks. It cannot be excluded that when the magma solidifies a phenomenon such as the Mullins-Sekerka instability also occurs. In our opinion the formation of columnar structures is unlikely to be related to a single passage of magma down the SF, and the "pencils" most likely form here after the passage of the SF, when the lava can already be regarded as solid. However it can be conjectured that the gas dissolved in the lava continues for a long time to flow up through the lava; this flow is described by the nonlinear equations of diffusion and heat conduction. This gas also carries heat with it, and as we shall show below it can itself form, owing to the nonlinearity of the flows, superheated paths with the structure of honeycombs, which subsequently give a stack of "pencils."

In concluding this introduction we point out that in many cases hexagonal cells arise by the well-known mechanism of "Bénard cells" in the process of convection of liquid in the field of gravity. Thus "structured soil" with traces of Bénard cells, which are active during the period when the crust of ice on the soil melts, is described in Ref. 7. However this mechanism of self-organization of flows will not be studied in this paper.

## 2. "UNILATERAL MODEL" FOR THE TEMPERATURE OR IMPURITY ON THE SOLIDIFICATION FRONT

We briefly reproduce some results of Ref. 4 which describe simultaneously two problems—the "temperature" and the "impurity" problems. Suppose that the solidification front moves downwards with constant velocity $v$ along a gas-saturated supercooled liquid. Then, in the system of coordinates where the front is at rest in the plane $z = 0$, we have the equation of heat conduction (for simplicity, we assume that the solid and liquid phases have the same density $\rho$, heat capacity $c_p$, and thermal conductivity $\varkappa$):

$$\rho c_p T_t' + \operatorname{div} \mathbf{q}^{(T)} = 0, \quad \mathbf{q}^{(T)} = -\varkappa \nabla T + \rho c_p T \mathbf{v}. \tag{2.1}$$

If $z = a(t, x, y)$ is the surface of the disturbed front, whose normal is

$$\mathbf{N} = (N_x, N_y, N_z), \; N_z = \nu = [1 + (\nabla a)^2]^{-1/2}, \; N_{x,y} = -\nu \nabla_{x,y} a, \tag{2.2}$$

then, taking into account the motion of the front itself with the velocity $\mathbf{v}_f = \mathbf{N} v_f$, where $v_f = \nu a_t'$, and the liberation of heat of fusion $Q$ on the front, we have on the front the boundary conditions that the temperatures are equal $T_1 = T_2 = T_3$ ($T_3$ is the solidification temperature) as well

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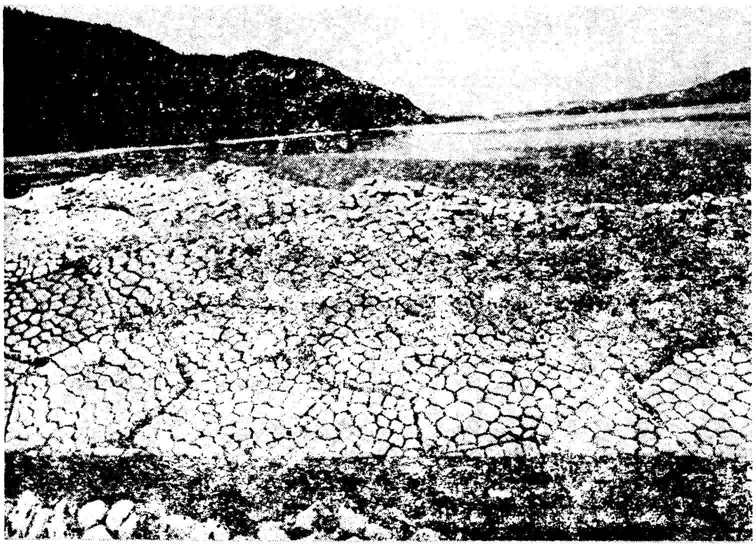

FIG. 1. Parquet of solidified lava and on Mys Stolbchatyĭ on Kunashir Island.

as the condition of correct matching of the jump of the heat fluxes

$$-\varkappa \mathbf{N}\nabla T_2 = -\varkappa \mathbf{N}\nabla T_1 + \rho Q(v - a_t')\mathbf{v}. \tag{2.3}$$

Here the index 1 refers to the liquid phase and the index 2 refers to the solid phase, and if in what follows for convenience we introduce the "penetration depth of heat," equal to $l = \varkappa/\rho c_p v$ as well as the dimensionless temperature $\tau = Tc_p/Q$, then the above system of equations can be written in the form

$$\begin{gathered} l\Delta\tau = \tau_z' + \frac{1}{v}\tau_t', \quad \tau_1^f = \tau_2^f = T_3 c_p/Q, \\ l[\mathbf{N}\nabla(\tau_1 - \tau_2)]^f = \left(1 - \frac{1}{v}a_t'\right)\mathbf{v}. \end{gathered} \tag{2.4}$$

The problem of the behavior of an impurity with concentration $n_{1,2}$, described by the diffusion equation for a moving medium

$$n_t' + \operatorname{div}\mathbf{q}_n = 0, \quad \mathbf{q}_n = -D\nabla n + n\mathbf{v} \tag{2.5}$$

also reduces to a system of equations of exactly the same form. In contrast to the heat fluxes which, owing to the liberation of the heat of fusion, have a discontinuity at the front, the impurity fluxes should be continuous and for this reason for them we have the boundary condition

$$-D\mathbf{N}\nabla n_2 = -D\mathbf{N}\nabla n_1 + (n_1 - n_2)(v - a_t')\mathbf{v}, \tag{2.6}$$

but in order to determine the ratio of the boundary values of the concentrations themselves $n_1$ and $n_2$ it should be noted that on the contact front of the media the chemical potentials of the media must be equal: $\mu_1(n_1) = \mu_2(n_2)$, where, generally speaking, the chemical potentials depend differently on the concentrations $n_{1,2}$. When the phases are in contact with one another for a long time complete thermodynamic equilibrium should be established in the system and the concentrations should take on equilibrium values $n_{1,2}^0$ such that the equality $\mu_1(n_1^0) = \mu_2(n_2^0) = \mu^0$, where $\mu^0$ is the common equilibrium chemical potential of both phases. Under these conditions, the corrections to the equilibrium chemical potentials $\tilde{\mu}(n) = \mu(n) - \mu^0$ rather than the concentrations should be regarded as the basic quantities sought. Setting $n = n^0 + \delta n$ and assuming the increments to be small, we have approximately $\tilde{\mu} = \mu_n' \delta n$, where for simplicity the derivatives $\mu_n' = \partial\mu/\partial n$ can be regarded as being the same for both phases. Under these conditions the corrections introduced above for the chemical potentials will satisfy the same equations (2.5) as the concentrations, but on the front they must now be equal to one another, as the temperatures were previously, and the condition (2.6) gives

$$\begin{gathered} -D\mathbf{N}\nabla\tilde{\mu}_2 = -D\mathbf{N}\nabla\tilde{\mu}_1 + \mu_n'\Delta_n^0(v - a_t')\mathbf{v}, \\ \Delta_n^0 = n_1^0 - n_2^0. \end{gathered} \tag{2.7}$$

If we now introduce the "diffusion length" $l = D/v$ and the dimensionless "chemical potential correction" $\tau = \tilde{\mu}/\Delta_n^0\mu_n'$, then we obtain once again the system of equations (2.4); this shows that both problems are equivalent.

In the absence of perturbations the solutions of the system (2.4) are the functions

$$\tau_1^0(z) = A + B\exp\left(\frac{z}{l}\right), \quad \tau_2^0(z) = C + E\exp\left(\frac{z}{l}\right), \tag{2.8}$$

where $A$, $B$, $C$, and $E$ are constants. The simplest case is obtained for $E = 0$, when the other coefficients are equal to $C = T_3 c_p/Q$, $B = 1$, and $A = C - 1$. This is the case that corresponds to the "unilateral model" which we shall examine below.

## 3. INSTABILITY OF AND STATIONARY PATTERNS ON THE SF

We note first that the requirement $E = 0$ in Eq. (2.8) leads to $A = C - 1 = (T_3 c_p/Q) - 1$, and since $A = T_1^0(z \to \infty)c_p/Q$, the temperature of the liquid far below the surface must have the strictly determined value $T_1^0(-\infty) = T_3 - (Q/c_p) > 0$, less than the melting temperature $T_m$; this corresponds to supercooling of the liquid. Thus value of $T_1^0(-\infty)$ ensures that the velocity of the front is constant, but it may not correspond to the actual experimental conditions. In addition, the condition $E = 0$ means that the temperature of the solid phase is exactly equal to the solidification temperature; this condition also is not always satisfied, so that the model under study is somewhat arbitrary, but it does make it possible to analyze easily the problem of the stability of the solidification front.

In such a model it can be assumed that there are no disturbances in the solid phase and that in the liquid phase $\tau_1 = \tau_1^0 + \tilde{\tau}$. Then from Eq. (2.4) we obtain the complete nonlinear system of equations for the corrections $\tilde{\tau}$:

$$v^{-1}\tilde{\tau}_t' + \tilde{\tau}_z' = l(\tilde{\tau}_{zz}'' + \Delta_\perp \tilde{\tau}), \quad \Delta_\perp \tilde{\tau} = \tilde{\tau}_{xx}'' + \tilde{\tau}_{yy}'',$$
$$\tilde{\tau}|_{z=a} = 1 - e^\alpha, \quad l(\tilde{\tau}_z' - \nabla_\perp \alpha \nabla_\perp \tilde{\tau})|_{z=a} = 1 - e^\alpha - \alpha_t' l/v, \tag{3.1}$$

where $\alpha = a/l$. In the linear approximation with $\alpha \ll 1$ we assume that

$$\alpha = \alpha_0(x, y)\exp(\gamma t), \quad \tau = -\alpha\exp(\beta z), \tag{3.2}$$

and then the last boundary condition (3.1) gives the relation $\beta = 1/l + \gamma/v$, and the main (first) equation in Eq. (3.1) assumes the form

$$(\gamma/v)^2\alpha_0(x, y) = -\Delta_\perp \alpha_0. \tag{3.3}$$

For $\alpha_0 \sim \cos(kx)$ Eq. (3.3) gives the growth rate $\gamma = |k|v$ of the instability of the solidification front. This instability is customarily called the "Mullins-Sekerka" instability.[2,4]

Here the short-wavelength perturbations grow most rapidly. In a more detailed calculation, however, the stabilizing effect of the surface tension forces should be taken into account, as done in Ref. 4, some results of which we presented above. Next, for simplicity we shall neglect them and we shall examine immediately the stationary case, which was not studied separately in Ref. 4. Setting in Eq. (3.1) $\alpha_t' = \tilde{\tau}_t' = 0$ and $\tilde{\tau} = \psi \exp(z/2l)$, we obtain for the function $\psi(x, y, z)$

$$\Delta\psi = \frac{\psi}{4l^2},$$
$$\psi|_{z=a} = -2\,\mathrm{sh}\frac{\alpha}{2} = 2l(\psi_z' - \nabla_\perp a \nabla_\perp \psi)_{z=a} = \frac{2l}{v}(\mathbf{N}\nabla\psi)_{z=a}. \tag{3.4}$$

This system can be reduced to an integral equation for the surface by noting that it has a very simple Green's function

$$G(\mathbf{R}) = \frac{1}{R}\exp\left(\frac{-R}{2l}\right), \quad \Delta G - \frac{G}{4l^2} = -4\pi\delta(\mathbf{R}), \quad \mathbf{R} = \mathbf{r} - \mathbf{r}_0, \tag{3.5}$$

using which it is easy to obtain the identity

$$\frac{1}{4\pi}\mathrm{div}(G\nabla\psi - \psi\nabla G) = \psi(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}_0). \tag{3.6}$$

Assuming that the point $\mathbf{r}_0$ lies inside the liquid and integrating over the entire volume of the liquid phase we express $\psi$ in terms of the boundary values:

$$\psi(\mathbf{r}_0) = \frac{1}{4\pi}\iint (G\nabla\psi - \psi\Delta G)\,d\mathbf{S}$$
$$= \frac{1}{4\pi}\iint\left[\frac{G}{v}(\mathbf{N}\nabla\psi) - \frac{\psi}{v}(\mathbf{N}\nabla G)\right]dx\,dy, \tag{3.7}$$

and in what follows we shall try to shift the point $\mathbf{r}_0$ onto the boundary $z = a_0(x_0, y_0)$; this should give the desired integral equation. In so doing, however, it is necessary to take into account one subtlety, namely, the fact that on the other side of the surface, i.e., in the solid phase, there are no disturbances, so that the integral $\int\psi\delta(\mathbf{R})dV$ should extend only over the hemisphere adjoining from below the boundary under study, and for this reason we have on the left-hand side in Eq. (3.7) only half of the boundary value of the "potential;" this gives

$$\frac{1}{2}\psi|_{z=a_0} = -\mathrm{sh}\frac{\alpha_0}{2} = \frac{1}{4\pi l}\iint \mathrm{sh}\frac{\alpha}{2}\left[2l\frac{\partial G}{\partial R}\right.$$
$$\left.\times\left(\frac{\mathbf{NR}}{vR}\right) - G\right]_{z_0\to a_0}^{z\to a} dx\,dy, \tag{3.8}$$

where $\mathbf{NR}/v = R_z - \mathbf{R}_\perp \nabla_\perp a = a - a_0 - \boldsymbol{\rho}\nabla_\perp a$, $\boldsymbol{\rho} = (x - x_0, y - y_0)$.

This integral equation is still quite complicated, and if numerical methods are not employed, it can be solved only approximately, assuming that the quantity $\alpha = a/l$ is small and retaining terms of order no higher than second-order infinitesimals, which is what we shall do below.

## 4. APPROXIMATE EQUATION FOR STATIONARY PATTERNS ON THE SF

With accuracy up to quadratic terms Eq. (3.8) can be rewritten in the form

$$\alpha_0 = \alpha(x_0, y_0)$$
$$= \frac{1}{4\pi l}\iint\left[\alpha G(\rho) + 2l^2\left(\alpha_0\alpha - \alpha^2 + \frac{\rho}{2}\nabla_\perp\alpha^2\right)\frac{\partial G(\rho)}{\rho\,\partial\rho}\right]dx\,dy, \tag{4.1}$$

where $G(\rho) = \rho^{-1}\exp(-\rho/2l)$ satisfies the relations

$$\frac{\boldsymbol{\rho}}{\rho}\frac{\partial G}{\partial\rho} = \nabla_\perp G, \quad \Delta_\perp G = \frac{G}{(2l)^2} - \frac{\partial G}{\rho\partial\rho}, \tag{4.2}$$

and for this reason Eq. (4.1) can be rewritten in the form

$$\alpha_0 - \hat{G}\alpha_0 = \frac{l}{2\pi}\iint\left[(\alpha_0\alpha - \alpha^2)\left(\frac{G}{(2l)^2} - \Delta_\perp G\right)\right.$$
$$\left.+\frac{1}{2}\nabla_\perp\alpha^2\nabla_\perp G\right]dx\,dy. \tag{4.3}$$

Here, for convenience we introduce the following notation for the integral operator:

$$\hat{G}\alpha(x, y) = \frac{1}{4\pi l}\iint \alpha(x', y')G(\rho = \mathbf{r}_\perp' - \mathbf{r}_\perp)\,dx'\,dy'. \tag{4.4}$$

Integrating by parts the terms containing derivatives of the function $G$, the result (4.3) can be put into the form

$$\alpha - \hat{G}\alpha = {}^1/_2\alpha(1 - 4l^2\Delta_\perp)\hat{G}\alpha - \hat{G}({}^1/_2\alpha^2 - l^2\Delta_\perp\alpha^2). \tag{4.5}$$

Next, we note that introducing the operator $\hat{G}^{-1}$ inverse to the operator $\hat{G}$, we obtain the equality $(1 - 4l^2\Delta_\perp) = (\hat{G}^{-1})^2$ and $(1 - 4l^2\Delta_\perp)\hat{G}\alpha = (\hat{G}^{-1})\alpha$. But from Eq. (4.5) we have, in the linear approximation, $\hat{G}^{-1}\alpha \approx \alpha$, and for this reason Eq. (4.5) can be rewritten in the form

$$\alpha - \hat{G}\alpha = {}^1/_2\alpha^2 - \hat{G}({}^1/_2\alpha^2 - l^2\Delta_\perp\alpha^2). \tag{4.6}$$

Finally, introducing the auxiliary function $\tilde{\alpha} = \alpha - \frac{1}{2}\alpha^2 + l^2\Delta_\perp\alpha^2$, which also describes approximately the surface of the solidification front, we obtain for it from Eq. (4.6) the equation

$$\tilde{\alpha} - \hat{G}\alpha = l^2\Delta_\perp\tilde{\alpha}^2. \tag{4.7}$$

Finally, this equation can also be obtained directly from the system (3.4) by writing the solution of the main equation (3.4) in the form

$$\psi(x,y,z)=\iint a_{\mathbf{k}}\exp\left\{i\mathbf{kr}+\frac{z}{2l}[1+(2kl)^2]^{1/2}\right\}d\mathbf{k}, \quad (4.8)$$

where $d\mathbf{k}=dk_1dk_2$, $\mathbf{kr}=xk_1+yk_2$. Hence we find the quantities

$$\psi|_{z=0}=\iint a_{\mathbf{k}}\exp(i\mathbf{kr})\,d\mathbf{k},$$

$$F=2l\psi_z'|_{z=0}=\iint a_{\mathbf{k}}[1+(2kl)^2]^{1/2}\exp(i\mathbf{kr})\,d\mathbf{k}, \quad (4.9)$$

which turn out to be related to one another by the integral operator introduced above: $\psi_0=\hat{G}F$. Next, expanding the boundary conditions (3.4) in powers of $\alpha\ll1$, we once again obtain Eq. (4.7).

For waves with long wavelengths the operator $\hat{G}$ can be represented in the form of a series:

$$G\tilde{\alpha}=(1-4l^2\Delta_\perp)^{-1/2}\tilde{\alpha}=(1+2l^2\Delta_\perp+6l^4\Delta_\perp^2+20l^6\Delta_\perp^3+\dots)\tilde{\alpha}. \quad (4.10)$$

However the short-wavelength disturbances are of greatest interest. For such disturbances, as is obvious from Eq. (4.9), the term $\hat{G}\tilde{\alpha}$ in Eq. (4.7) can be approximately completely neglected. This leads to the equation

$$l^2\Delta_\perp\tilde{\alpha}^2=\tilde{\alpha}, \quad (4.11)$$

which we shall examine.

In the one-dimensional case the solution of Eq. (4.11) is the function

$$\tilde{\alpha}=-|\alpha_0|(1-\cos\varphi)^{1/3},\quad \int_0^{\varphi}(1-\cos\beta)^{1/6}d\beta=\frac{x}{l}\left(\frac{3}{|\alpha_0|}\right)^{1/2}. \quad (4.12)$$

If the expression $(1-\cos\beta)^{1/6}$ is replaced by its approximate average value

$$\langle(1-\cos\beta)^{1/6}\rangle\approx\frac{3}{\pi^2}\left(\frac{3}{2}\right)^{1/2}\left[\Gamma\left(\frac{2}{3}\right)\right]^3=1{,}003, \quad (4.13)$$

then for the solution (4.12) we obtain

$$\alpha(x)=-3(kl)^{-2}(1-\cos kx)^{1/3},\quad \alpha_{\max}=3\cdot2^{1/3}(kl)^{-2}. \quad (4.14)$$

A graph of the function $f=[1-\cos(kx)]^{1/3}$ is shown by the dashed lines in Fig. 2b, where the solid line shows the profile of the solidification front, observed in Jackson's experiments[5] with supercooled melt of liquid $CBr_4$. As we can see, here the agreement between theory and experiment is good, so that Jackson's front is described, with good accuracy, by the formula

$$a(x)=\frac{3}{2}\lambda\left[\frac{1}{2}\left(1-\cos\frac{2\pi x}{\lambda}\right)\right]^{1/3},\quad \lambda\approx2\cdot10^{-3}\text{ cm}. \quad (4.15)$$

The unilateral model employed above is not the only model. It is possible to use a different approach (see, for example, Refs. 8–10), in which the interphase boundary, moving with constant velocity, satisfies an equation of the type

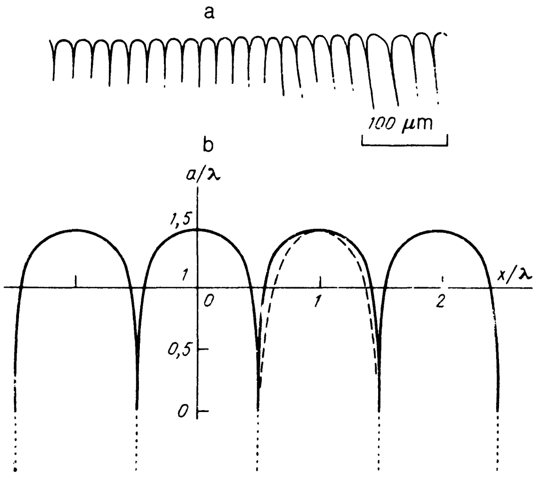


FIG. 2. Solidification front of liquid $CBr_4$ in Jackson's experiments:[5] a) for a 25 μm thick layer of liquid between two glass sheets, b) enlarged scheme of the front: solid line—numerical calculation from Ref. 4; dashed line—the formula (4.15).

$$\Delta=\frac{1}{2\pi l}\int_{-\infty}^{+\infty}\exp\left[\frac{a(x)-a(x')}{2l}\right]K_0\left(\frac{\rho}{2l}\right)dx', \quad (4.16)$$

$$\rho^2=(x-x')^2+[a(x)-a(x')]^2,\quad \Delta\equiv(T_3-T_{-\infty})c_p/Q.$$

Here $K_0$ is the modified Bessel function, and for simplicity, as done everywhere above, the contribution of surface tension, which is taken into account in Refs. 7–9, is neglected. An equation of this form was used previously in Ivantsov's theory of dendrites, but it is also applicable in the two-dimensional problem of the form of the solidification front. Although Eq. (4.16) differs from Eq. (3.8), it nonetheless gives similar results. Namely, a flat front ($a=0$) is possible only for $\Delta=1$, i.e., $T_{-\infty}=T_3-Q/C_p$, and under this condition the expansion in powers of the amplitude once again gives Eqs. (4.7) and (4.11) with the approximate solution (4.15); now, however, the equations are one-dimensional. For $\Delta\neq1$, then there is no solution in the form of a flat front, but solutions of the type Saffman-Taylor "fingers" ($\lambda=$ const)

$$a(x)=-\lambda\frac{1-\Delta}{\pi}\ln\left|\cos\frac{\pi x}{\lambda\Delta}\right|,\quad \Delta<1, \quad (4.17)$$

in the limit $l\to\infty$, and similar solutions[9] are possible. They describe periodic sequences of dendrites, separated by slowly (logarithmically) narrowing "interlayers" of the liquid phase. In Jackson's experiments, whose results are shown in Fig. 2, such "interlayers" are not observed. After a significant amount of impurity (several percent) is added dendrites grow on the front.[5]

## 5. "PARQUET" OF HEXAGONS ON THE SOLIDIFICATION FRONT

In Jackson's experiments a one-dimensional solidification front was artificially formed between close parallel sheets of glass. In the absence of close boundaries, however, there should form on a flat SF disturbances in the form of a hexagonal parquet, approximately described by the formula

$$\tilde{\alpha}=A\sigma_0,\quad \sigma_0(x,y)=\cos\varphi_1+\cos\varphi_2+\cos\varphi_3,$$
$$\varphi_i=k\mathbf{n}_i\mathbf{r}_\perp, \quad (5.1)$$

where $\mathbf{n}_{1,2,3}$ are three two-dimensional unit vectors whose sum is zero: $\mathbf{n}_1 + \mathbf{n}_2 + \mathbf{n}_3 = 0$. The square of the function $\alpha(x,y)$ is equal to

$$\tilde{\alpha}^2 = A^2\sigma_0^2, \quad \sigma_0^2 = {}^3/_2 + \sigma_0 + \sigma_1 + {}^1/_2\sigma_2,$$
$$\sigma_2 = \cos 2\varphi_1 + \cos 2\varphi_2 + \cos 2\varphi_3, \tag{5.2}$$
$$\sigma_1 = \cos(\varphi_1 - \varphi_2) + \cos(\varphi_1 - \varphi_3) + \cos(\varphi_2 - \varphi_3)$$

and contains the "resonance" term $\sigma_0$. Neglecting the nonresonance terms $\sigma_{1,2}$ and substituting the expressions (5.1) and (5.2) into Eq. (4.11), we find the amplitude $A = -(kl)^{-2}$. If we attempted to find a solution with a parquet consisting of quadrangles, approximately described by the function $\tilde{\alpha} = A(\cos kx + \cos ky)$, then the square of this term would not give a "resonance" term, and for this reason in our approximation, which takes into account only quadratic corrections, a solution consisting of quadrangles cannot arise. This situation is close to the picture of the appearance of a "parquet" on a surface (see Ref. 11) of an oscillating liquid, where, owing to the parametric resonance between oscillations of the bottom and surface waves, there first arises with a small amplitude a parquet consisting of hexagons, after which a larger amplitude a parquet develops consisting of quadrangles, and finally, with an even larger amplitude, a Parquet develops consisting of one-dimensional rolls.

The solution (5.1) is approximate, but it can be refined by seeking within the boundaries of one cell a solution in the form of an expansion in powers of the radius:

$$\tilde{\alpha} = \sum_0^\infty a_n(\varphi) r^{2n}.$$

The square of this sum is equal to

$$\tilde{\alpha}^2 = \sum_0^\infty S_n(\varphi) r^{2n}, \quad S_n(\varphi) = \sum_{l+m=n} a_l a_m. \tag{5.3}$$

Substituting these expressions into Eq. (4.11) we obtain the recurrence equations

$$S_n''(\varphi) + 4n^2 S_n = l^{-2} a_{n-1}(\varphi), \quad n = 1, 2, 3, \ldots, \quad a_0 = \text{const.} \tag{5.4}$$

Note that a similar expansion for the function $\sigma_0$ has the form

$$\sigma_0 = \sum_0^\infty \beta_n r^{2n},$$

$$\beta_n = \frac{(-k^2)^n}{(2n)!}\{[\cos\varphi]^{2n} + [\cos(\varphi+60^\circ)]^{2n} + [\cos(\varphi-60^\circ)]^{2n}\}, \tag{5.5}$$

where $\beta_0 = 3$, $\beta_1 = -3k^2/4$, $\beta_2 = 3k^4/64$, and the dependence on $\varphi$ starts with $\beta_3$:

$$\beta_3 = \frac{-k^6}{6!64}(8\cos 6\varphi + 6\cos 4\varphi + 19\cos 2\varphi + 40). \tag{5.6}$$

If we write $x_0 = (kr/2)^2$, then the expression (5.5) assumes the form

$$\sigma_0 = 3\Big[1 - x_0 + \frac{1}{4}x_0^2 - \frac{x_0^3}{54}\Big(1 + \frac{19}{40}\cos 2\varphi + \frac{6}{40}\cos 4\varphi + \frac{8}{40}\cos 6\varphi\Big) + \ldots\Big]. \tag{5.7}$$

Analogously, in our solution for a cell we set $a_0 = -|a_0|$, and denoting $x = r^2/8l^2|a_0| > 0$, we write in the following form the solution obtained from Eq. (5.4):

$$\tilde{\alpha} = -|a_0|[1 - x - {}^1/_4x^2 - {}^2/_9x^3(1 + A\cos 6\varphi) + \ldots], \tag{5.8}$$

where $A$ is an arbitrary constant. It is simplest to set here $A = -1$, and if it is assumed that $x_0 = x$, then we find $|a_0| = 1/2k^2l^2$ and

$$\tilde{\alpha} = \frac{-1}{2k^2l^2}\Big(1 - x - \frac{1}{4}x^2 - \frac{4}{9}x^3\sin^2 3\varphi + \ldots\Big). \tag{5.9}$$

This series for a cell can be continued.

## 6. "VOLUME" MECHANISM OF FORMATION OF COLUMNAR ROCK STRUCTURES

The "surface" mechanism described above explains well the appearance of "pencil structures" on the surface of a moving solidification front in the process of growth of crystals from supercooled melt. In experiments it is easy to create conditions of supercooling by appropriately adjusting the heater settings and, vice versa, to exclude supercooling so that such a Mullins-Sekerka instability and pencil structures would not arise. We cannot exclude the possibility that this mechanism also results in the formation of "pencil structures" in a cooling volcanic lava.

In our opinion, however, in a lava it is difficult to imagine the appearance of a supercooled layer whose temperature would be lower than the temperature both above and below this layer. An exception could be concentration supercooling, but its presence does not always result in instability of the front. For this reason, in what follows we shall study a different mechanism, not a surface but rather a "bulk" mechanism, for the appearance of rock "pencil structures" of the "columnar" type and "stacks."

It can be conjectured that, in contrast to crystals, in a cooling magma the process of liberation of gas, primarily water molecules and sulfur dioxide, dissolved in the magma plays a significant role in the cooling magma.

We describe this process by the diffusion equation

$$n_t' + \operatorname{div}\mathbf{q}_n = 0, \quad \mathbf{q}_n = -D\nabla n, \tag{6.1}$$

in which, however, we assume that the diffusion equation $D$ is temperature dependent. As is well known, for molecular diffusion (see, for example, Ref. 12) this dependence is approximated well by the empirical formula

$$D(T) = D_0 \exp(-Q/k_B T),$$

where $Q$ is the activation energy. Since $D(T)$ increases with temperature, it can be expected that the escaping gas will form for itself more thoroughly heated channels, and this can result in instability. The empirical formula presented above, however, is too complicated for our purposes, and we shall replace it with a simpler formula of the form $D(T) = D_{-\infty}T/T_{-\infty}$, where $T_{-\infty}$ is the temperature of the deep magma below. We note that at $T = 0$ both formulas give $D = 0$, but we shall study comparatively small variations of the temperature. In addition, the solidifying magma can have a significant porosity, raising the effective diffusion coefficient above the molecular value.

It is also necessary to take into account the fact that the rising gas itself transports heat, and for this reason we shall write the heat conduction equation in the form

$$\rho c_p T_t' + \text{div}\, \mathbf{q}_T = 0, \quad \mathbf{q}_T = -\varkappa \nabla T + \frac{kT}{\gamma_\Gamma - 1} \mathbf{q}_n, \qquad (6.2)$$

where $\gamma_\Gamma = \gamma_{\text{gas}} = c_p/c_v$, and $k_B T/(\gamma_\Gamma - 1)$ is the energy transported by one molecule of gas. Introducing the dimensionless temperature $\tau = T/T_{-\infty}$ and the thermal diffusivity $\chi = \varkappa/\rho c_p$, we rewrite Eq. (6.2) in the form

$$\chi^{-1}\tau_t' - \Delta\tau + \text{div}\,[\mathbf{q}_n \tau k/\varkappa(\gamma_\Gamma - 1)] = 0, \qquad (6.3)$$

and taking the gradient of Eq. (6.1) and writing, for brevity, $\mathbf{q}_n^0 = -D_{-\infty}\nabla n$, we represent Eq. (6.1) in a form convenient for our purposes:

$$\frac{\partial}{\partial t}\mathbf{q}_n^0 = D_{-\infty}\nabla\, \text{div}\, \mathbf{q}_n, \quad \mathbf{q}_n = \tau \mathbf{q}_n^0. \qquad (6.4)$$

In order to simplify as much as possible the formulation of the problem, we assume that in the stationary undisturbed state the temperature is everywhere equal to the value $T_{-\infty}$, so that $\tau = 1$, and the diffusion flux of gas is also constant and has some value $q_{00}$, artificially maintained constant as a result of prolonged injection of gas from deep inside the magma, which in our formulation is regarded to be a single-phase motionless medium without any solidification front. We shall show below that such a stationary state is unstable: random acceleration of the transport of hot gas increases the temperature locally, which in turn accelerates the process even more.

It should be emphasized that our formulation of the problem is somewhat artificial. For example, Eqs. (6.3) and (6.4) can have a different stationary solution with a constant gas flux $q_n = q_{00}$, but with variable temperature, also satisfying Eq. (6.3):

$$T = T_{-\infty} - (T_{-\infty} - T_0)\exp(z/l), \quad l = \varkappa(\gamma_\Gamma - 1)/k_B q_{00}. \qquad (6.5)$$

Here $T_0$ is the temperature at the surface $z = 0$, $k_B$ is Boltzmann's constant, and $l$ is the characteristic cooling length. However, we assumed that $T_0 = T_{-\infty}$, and this assumption is essentially equivalent to the assumption made in the "unilateral model" for the solidification front.

## 7. INSTABILITY AND FILAMENTATION OF NONLINEAR HEAT AND GAS FLOWS

For brevity we introduce the notation for the vector $\mathbf{q} = \mathbf{q}_n^0/q_{00}$ and rewrite again Eqs. (6.3) and (6.4) in the form

$$\chi^{-1}\tau_t' - \Delta\tau + \text{div}\,(\tau^2 \mathbf{g}/l) = 0, \quad \mathbf{g}_t' = D_{-\infty}\nabla\,\text{div}\,(\tau\mathbf{g}) \qquad (7.1)$$

with unperturbed solutions $\tau_0 = 1$; here $\mathbf{g}_0 = \mathbf{I}_z$ is a unit vector. In order to investigate the stability we set $\tau = \tau_0 + \tau_1$ and $\mathbf{g} = \mathbf{g}_0 + \mathbf{g}_1$, making the assumption that the quantities $\tau_1$ and $\mathbf{g}_1$ are small. Then in the linear approximation we obtain from Eq. (7.1)

$$(l/\chi)\tau_{1t}' - l\Delta\tau_1 + \text{div}\,(\mathbf{g}_1 + 2\tau_1\mathbf{g}_0) = 0,$$
$$\mathbf{g}_{1t}' - D_{-\infty}\nabla\,\text{div}\,(\mathbf{g}_1 + \tau_1\mathbf{g}_0) = 0. \qquad (7.2)$$

The simplest model variant of the solution is obtained if, first, it is assumed that the diffusion coefficients $D_{-\infty}$ and the thermal diffusivity $\chi$, which have the same dimension, are equal to one another and, second, it is assumed that the corrections $\tau_1$ and $\mathbf{g}_1$ depend exponentially on the coordinate $z$ [$\propto \exp(z/l)$] with the same characteristic length $l$ as in Eq. (6.5), so that we seek the solutions in the form (for $z<0$)

$$\tau_1 = \alpha(t, x, y)\exp\left(\frac{z}{l}\right), \quad \text{div}\,\mathbf{g}_1 = \frac{\beta(t, x, y)}{l}\exp\left(\frac{z}{l}\right) \qquad (7.3)$$

and substituting them into Eq. (7.2) we obtain

$$\alpha + \beta = l^2\left(\Delta_\perp\alpha - \frac{1}{\chi}\alpha_t'\right), \quad (\alpha+\beta)_t' = \chi\Delta_\perp(2\alpha + \beta). \qquad (7.4)$$

Hence for solutions of the form $\alpha \propto \exp[\gamma t + i(xk_1 + yk_2)]$ we obtain the growth rate of the instability $\gamma = (|\mathbf{k}| - l|\mathbf{k}|^2)\chi/l$, which has the maximum value $\gamma_{\max} = \chi/4l^2$ for $|\mathbf{k}| = 1/2l$, which corresponds to the wavelength

$$\lambda_\perp = 4\pi l = 4\pi\varkappa(\gamma_\Gamma - 1)/k_B q_{00}. \qquad (7.5)$$

Thus the fastest growing perturbations are of the form

$$\tau_1 = A\sigma(x, y)\exp\left(\frac{z + vt}{l}\right), \quad v = \frac{\chi}{4l} = \frac{k_B q_{00}}{4\rho c_p(\gamma_\Gamma - 1)},$$
$$\sigma(x, y) = \sum_j \cos\left(\frac{\mathbf{n}_j\mathbf{r}}{2l}\right), \qquad (7.6)$$

which advance downwards along the magma with velocity $v$, proportional to the gas flux, and give "nuclei" of blocks with the diameter (7.5), which is inversely proportional to the gas flux. If quadratically small terms were taken into account, "pencils" with a hexagonal cross section would be obtained.

## 8. DISCUSSION

The applicability of the above "bulk" mechanism of filamentation to a cooling magma is difficult to check, because no direct observations have been made. Up to now geologists have explained the formation of "columnar structures" primarily on the basis of the phenomenon of compression (contraction) of lava as the lava cools under certain conditions: with moderate viscosity of lava whose composition corresponds to basalts and andesite-basalts, and with gradual and uniform cooling of the lava.[12] In Ref. 6 it is pointed out that when a basalt dike cools from a temperature of 1000 °C to 25 °C a 100 m length shrinks by 25 cm, so that a crack accounts for 1/400th of the length. In the same book, on page 221 a photograph of the "Giants Causeway" in Northern Ireland is also presented (Fig. 7–33 in Ref. 6). The condition of uniform cooling of lava is evidently realized in underwater[12] and under-ice[13] eruptions or when intrusions cool in closed volumes,[14] which gives rise to the appearance of a thermal screen in the upper layers of lava. In reality columnar structures form in dark lavas of different viscosity—ranging from olivine basalts in the region of the Vilyuchinskii volcano on Kamchatka[12] to hornblende andesites of Plotin's extrusions[15] and dacitic liparites of Mys Stolbchatyĭ.[16]

Using for the thermophysical parameters of basalts[17] the approximate values $\rho = 2.6$ g/cm$^3$, $c_p = 0.2$ cal/g·deg, and $\varkappa = 5.2\cdot 10^{-3}$ cal/cm·s·deg or for the more viscous andesite-dacitic rocks $\rho = 2.49$ g/cm$^3$, $c_p = 0.2$ cal/g·deg, and $\varkappa = 5.7\cdot 10^{-3}$ cal/cm·s·deg, we find the typical thermal diffusivity of lava $\chi = \varkappa/\rho c_p = 10^{-2}$ cm$^2$/s. According to data given by different authors, the diffusion coefficients of the emanations in rocks vary over wide limits $10^{-2}$–$10^{-4}$ cm$^2$/s and depend on the porosity, water saturation, temperature, and sorption properties of the rock.[18] It has not been excluded that effusive or extrusive lavas reaching the surface have significant porosity, which increases by two to three orders of magnitude the effective diffusion coefficient of gases, as has been found for rocks near pipes.[19] For this reason the model assumption which we have made, that $\chi$ is equal to $D_{-\infty}$, can be approximately satisfied.

The hexagonal "pencils" on Mys Stolbchatyĭ (Fig. 1) have a diameter of 20 cm, and if it is assumed that this diameter is equal to the wavelength (7.5), then taking for water the value $\gamma_\Gamma = 1.2$ and Boltzmann's constant $k_B = 3.38\cdot 10^{-24}$ cal/deg, we find that the formation of "pencils" with such a diameter requires a gas flux density $q_{00} = 4\pi\varkappa(\gamma_\Gamma - 1)/k_B\lambda_\perp = 2\cdot 10^{20}$ molecules/cm$^2$·s $= 6\cdot 10^{-3}$ g/cm$^2$·s. For such a flow of vapor "pumped" through the magma the "honeycombs" should grow downwards at a rate $v = \chi/4l = 5.65$ cm/h $= 1.35$ m/day, so that over a period of one month the "honeycombs" will grow to a depth of 40 m. Such estimates of the rates of formation of nuclei of boundaries of blocks, which are ultimately formed owing to the contraction of rocks during prolonged cooling, seem reasonable to us. It is also helpful to note that in the mechanism which we have adopted the maximum growth rate is determined not by surface tension but rather by the same diffusion. When surface tension is taken into account the estimates of the dominant wavelength are incorrect, even when constructing a theory of growth of dendritic crystals (see Ref. 4). In magma, however, with relatively large diameters of "pencils" ($\sim$50 cm in the Giants Causeway) it is very difficult to expect that the effect of these forces will be significant.

In our opinion the effect of contraction undoubtedly is important, but because of the purely mechanical fragmentation regular columns with a length-to-diameter ratio of the order of 100 are unlikely to grow. Cracks evidently grow along existing boundaries of the "honeycombs," formed by the above mechanism of filamentation of nonlinear heat and gas flows. It is this mechanism that is primarily responsible for the formation of the "columnar structures" and stacks. However this problem requires further study.

Finally, we note that purely theoretically the nonlinear instability, studied in the first sections above, of the solidification front usefully supplements the nonlinear descriptions, which we gave earlier in other works, of the instability of other hydrodynamic discontinuities, namely, velocity shear[20] ("Kelvin-Helmholtz instability"), flute instability of shock waves[21] ("D'yakov instability"), Rayleigh-Taylor instability of the jump in the density of two liquids in a gravitational field,[22] instability of a flame front[23] ("Landau–Zel'dovich instability"), and finally instability of the front of many types of solitons[24] (see also Ref. 22).

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