SPATIALLY PERIODIC NONSTATIONARY PROCESSES ACCOMPANYING CRYSTALLIZATION

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There are a large number of both theoretical and applied studies of the possible mechanisms for the appearance of nonuniformity, including striated nonuniformity, in the impurity distribution in a growing crystal. The theoretical works are concerned, as a rule, with the dependence of the distribution factors on the oscillations of the temperature (or concentration) field in the mother phase near the interphase boundary. The nonuniformity of the impurity distribution, occurring as a result of a loss of morphological stability of the growing face and the appearance of a cellular structure, has been studied in numerous works by Sekerka and his co-workers [1]. They, however, made a traditional mathematical study of the stability of the solution of Stefan's problem. At the same time, experimental studies [2] of samples produced by epitaxy of GaAs from the gas phase, have demonstrated the fundamental character of the possible spatially periodic nonstationary processes occurring on the crystallization front in some apparently extreme regimes of growth of the crystals. A mechanism for loss of morphological stability, owing to the increasing role of thermal fluctuations of the parameters of the state of the system at the interphase boundary, is proposed in [3]. The purpose of this work is to extend the approach of [3] to study the possible effect of heat and mass transfer processes in the mother (liquid or gas) phase on the crystallization processes.

1. Effect of Convection on the Stability of a Flat Crystallization Front. We shall study the stability of directed crystallization of a binary alloy with natural convection under conditions of microgravity and on earth. The computational results were obtained based on the experimental of [4] on the crystallization of Al–Cu alloys with low copper concentrations ($\lesssim 0.1\%$) in the liquid phase. Good contact between the melt and the walls of the ampul was provided during the experiments. Therefore the convective flow, arising due to the dependence of the surface tension on the temperature and copper concentration in the melt (Marangoni convection), can be neglected. Accordingly, while studying the morphological stability of the interphase boundary, in this paper we examine the effect of natural convection on the kinetics of the long-wavelength part of the spectrum of locally equilibrium thermal fluctuations of a flat crystallization front. The effect of these fluctuations is determined in the general case by the thickness δ_D and δ_T of the diffusion and temperature boundary layers. They are evaluated from the relations [5]

$$\delta_T = \frac{\delta_0}{\sqrt[3]{\mathrm{Pr}}}, \quad \delta_D = \frac{\delta_0}{\sqrt[3]{\mathrm{Pr}_D}}, \quad \delta_0 \simeq \frac{3}{2}\sqrt{\frac{\eta l}{\rho v_0}},$$

where η is the dynamic viscosity, ρ is the density of the melt, D is the coefficient of diffusion of the impurity, ℓ and v_0 are the characteristic size and flow velocity of the melt near the crystallization front, $\mathrm{Pr}_D = \eta/\rho D$; $\mathrm{Pr} = \eta/\rho\chi_0$; and χ_0 is the thermal diffusivity of the melt.

The condition of complete mixing of the components of the melt is imposed outside the diffusion boundary layer, so that the copper concentration in this region is assumed to be given. Inside the diffusion layer the mass transfer to the interphase boundary is determined by molecular diffusion. Since for metals $\delta_T \gg \delta_D$ in performing the calculations we shall assume that the thickness δ_T is infinite.

The heat and mass transfer processes in the system (both regular and their fluctuation components determined by the thermal fluctuations) are described by the phenomenological heat conduction and diffusion equations, on whose right sides random external forces are forced:

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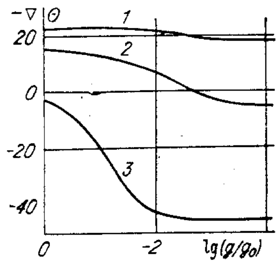

Fig. 1

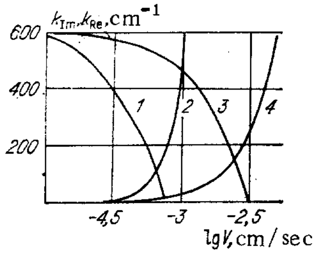

Fig. 2

$$\frac{\partial T_\nu}{\partial t} = V\frac{\partial T_\nu}{\partial z} + \chi_\nu \Delta T_\nu - \frac{1}{c_{p,\nu}\rho_\nu}\operatorname{div}\mathbf{q}^{\mathrm{st}}_{T_{\nu},i}\,(\nu = 0,1); \tag{1.1}$$

$$\frac{\partial c}{\partial t} = V\frac{\partial c}{\partial z} + D\Delta c - \operatorname{div}\mathbf{q}^{\mathrm{st}}_{D}. \tag{1.2}$$

Here the index ν denotes the liquid ($\nu = 0$) and solid ($\nu = 1$) phases, so that T_0 and T_1 are the temperature in the melt and in the crystal; c is the copper concentration in the melt; and, c_p, ρ, χ are the specific heat capacity, density, and coefficient of thermal diffusivity.

The external random forces determine the white-noise intensity of the locally equilibrium thermal fluctuations in the system. Their spectral characteristics are determined by the fluctuation–dissipation theorem [6]

$$\langle q^{\mathrm{st}}_{T,i}(\mathbf{r}, t)\, q^{\mathrm{st}}_{T,j}(\mathbf{r}', t')\rangle = 2k_{\mathrm{B}}\langle T\rangle^2 \varkappa\delta(\mathbf{r}-\mathbf{r}')\,\delta(t-t')\,\delta_{ij}; \tag{1.3}$$

$$\langle q^{\mathrm{st}}_{D,i}(\mathbf{r}, t)\, q^{\mathrm{st}}_{D,j}(\mathbf{r}', t')\rangle = \frac{2k_{\mathrm{B}}\langle T\rangle}{\rho_0^2}\gamma_D\delta(\mathbf{r}-\mathbf{r}')\,\delta(t-t')\,\delta_{ij}, \tag{1.4}$$

where $\varkappa$ is the coefficient of thermal conductivity; γ_0 is the kinetic coefficient of diffusion; k_B is Boltzmann's constant; $\delta(\mathbf{r}-\mathbf{r}')$ and $\delta(t - t')$ are Dirac delta functions; $\delta_{i,j}$ is the Kronecker delta function; and, <...> denotes averaging over an ensemble. Equations (1.1) and (1.2) are written in a coordinate system moving along the axis of the ingot with the velocity at which the ingot is drawn V. We shall represent the temperature and concentration fields and the relief function of the interphase boundary $\varepsilon(x, y, t)$ as sums of regular and fluctuation components $T = \langle T\rangle + \tilde{T}$, $c = \langle c\rangle$, $\varepsilon = \langle\varepsilon\rangle + \tilde{\varepsilon}$, so that $\langle\tilde{T}\rangle = \langle\tilde{c}\rangle = \langle\tilde{\varepsilon}\rangle = 0$. The crystallization velocity $V = d\langle\varepsilon\rangle/dt$. The conditions on the crystallization front are as follows:

$$T_0|_{z=\varepsilon} = T_1|_{z=\varepsilon},\quad \varkappa_1\frac{\partial T_1}{\partial n}\bigg|_{z=\varepsilon} - \varkappa_0\frac{\partial T_0}{\partial n}\bigg|_{z=\varepsilon} = \rho_1 q\frac{\partial\varepsilon}{\partial t},$$

$$D\frac{\partial c}{\partial n}\bigg|_{z=\varepsilon} = -(1-m)\frac{\partial\varepsilon}{\partial t}c\bigg|_{z=\varepsilon}.$$

Here $\partial/\partial n$ is the derivative along the normal to the interphase boundary; q is the specific heat of melting; m is the distribution factor of the impurity (for Al–Cu $m < 1$). The experiments of [4] on the study of morphological stability were performed for low impurity concentrations $c \leq 0.1\%$. Therefore the equation of the liquidus of the equilibrium phase diagram can be approximated by the linear dependence

$$T_0^{eq} = T_{eq} - nc|_{z=\varepsilon}.$$

Assuming that the growth mechanism is normal, we shall represent the local velocity of the interphase boundary as

$$\frac{\partial\varepsilon}{\partial t} = k\,(T_{eq} - nc|_{z=\varepsilon} - T_0|_{z=\varepsilon}) + \Gamma K(x, y, t),$$

where k is the kinetic growth factor; $\Gamma = k\sigma\langle T\rangle/\rho_1 q$; σ is the surface tension; and, K(x, y, t) is the local curvature of the crystallization front.

Heat transfer between the lateral surface of the sample and an ampul with radius R is determined by Newton's law

$$\varkappa_v \frac{\partial T_v}{\partial r}\bigg|_{r=R} = -\alpha(T_v - T_h).$$

Here T_h is the temperature at the heater and α is the coefficient of thermal conductivity. The temperature gradient $\partial T_h/\partial z = G_h$ at the faces of the sample in the crystal ($z = \langle\varepsilon\rangle - \ell_1$) and in the melt ($z = \langle\varepsilon\rangle + \ell_0$) is assumed to be constant and given:

$$\frac{\partial T_1}{\partial z}\bigg|_{z=\langle\varepsilon\rangle-l_1} = \frac{\partial T_0}{\partial z}\bigg|_{z=\langle\varepsilon\rangle+l_0} = G_h.$$

At the boundary of the diffusion boundary layer

$$c\big|_{z=\langle\varepsilon\rangle+\delta_D} = c_0$$

(c_0 is the impurity concentration in the core of the melt). For the temperature and concentration fields averaged over the ensemble the solution of the one-dimensional problem has the form

$$\langle c\rangle = \frac{\left\{m + (1-m)\exp\left[-\frac{V}{D}(z - \langle\varepsilon\rangle)\right]\right\}c_0}{\left[m + (1-m)\exp\left(-\frac{V}{D}\delta_D\right)\right]}; \tag{1.5}$$

$$\langle T_0\rangle = T_h(z) + \frac{VR\rho_0 c_{p,0}}{2\alpha}G_h + \frac{A_0}{2\,\mathrm{sh}(a_0 l_0)}\times$$
$$\times\left\{\frac{\exp(-a_0 l_0)}{a_0 - b_0}\exp[(a_0 - b_0)(z - \langle\varepsilon\rangle)] + \frac{\exp(a_0 l_0)}{a_0 + b_0}\exp[-(a_0 + b_0)(z - \langle\varepsilon\rangle)]\right\}; \tag{1.6}$$

$$\langle T_1\rangle = T_h(z) + \frac{VR\rho_1 c_{p,1}}{2\alpha}G_h + \frac{A_1}{2\,\mathrm{sh}(a_1 l_1)}\left\{\frac{\exp(a_1 l_1)}{(a_1 - b_1)}\times\right.$$
$$\left.\times\exp[(a_1 - b_1)(z - \langle\varepsilon\rangle)] + \frac{\exp(-a_1 l_1)}{a_1 + b_1}\exp[-(a_1 + b_1)(z - \langle\varepsilon\rangle)]\right\}, \tag{1.7}$$

where $a_i = \sqrt{b_i^2 + \frac{2\alpha}{R\varkappa_i}}$; $b_i = \frac{V}{2\chi_i}$;

$$A_0 = \frac{V}{\varkappa_0}\,\frac{\rho_1 q[a_1\,\mathrm{cth}(a_1 l_1) + b_1] - G_h(\rho_0 c_{p,0} - \rho_1 c_{p,1})}{a_0\,\mathrm{cth}(a_0 l_0) - b_0 + a_1\,\mathrm{cth}(a_1 l_1) + b_1};$$

$$A_1 = \frac{V}{\varkappa_1}\,\frac{\rho_1 q[a_0\,\mathrm{cth}(a_0 l_0) - b_0] + G_h(\rho_0 c_{p,0} - \rho_1 c_{p,1})}{a_0\,\mathrm{cth}(a_0 l_0) - b_0 + a_1\,\mathrm{cth}(a_1 l_1) + b_1}.$$

The expressions (1.5)-(1.7) enable evaluation of the magnitude of the concentration supercooling in front of the crystallization front. Figure 1 shows the dependence of $\nabla\Theta$ – the supercooling gradient in the melt at the interphase boundary – on the magnitude of the acceleration of gravity g. Here $\nabla\Theta = \frac{d\Theta}{dz}\Big|_{z=\langle\varepsilon\rangle}$, $\Theta = T_0^{eq} - \langle T_0\rangle$ and $g_0 = 9.81$ m/sec²; curves 1-3 were obtained for drawing velocities of the ingot $V = 10^{-4}$, 10^{-3}, and $3\cdot10^{-3}$ cm/sec. The copper concentration in the core of the melt was set equal to 0.1%, and the magnitude of the temperature gradient at the surface of the sample was set equal to 1300 deg/m.

We shall seek the solution of the problem for the fluctuation components of the temperature $\tilde{T}_i$, the copper concentration in the melt $\tilde{c}$, and the relief of the interphase boundary $\tilde{\varepsilon}(x, y, t)$ in the ω-**k** Fourier representation with respect to the time and spatial coordinates x, y. We obtain the equation for these components by subtracting the equations for the regu-

$\langle T_v \rangle$, $\langle c \rangle$ from (1.1) and (1.2). In the linear approximation of noninteracting fluctuations expressions were derived for $\tilde{\varepsilon}(\mathbf{k}, \omega)$ in the form of functionals of the random external forces. Application of the fluctuation-dissipation theorem (1.3) and (1.4) makes it possible to find the spectral densities of the pair correlation functions of the relief of the crystallization front. In the region of wave vectors realized in the course of the experiment [4]

$$\langle \tilde{\varepsilon}^2 \rangle_{k,\omega} \simeq \left[2|k| k_{\mathrm{B}} \langle T^2 \rangle (\varkappa_1 + \varkappa_0) + \frac{2n^2 (\varkappa_1 + \varkappa_0)^2 |k| k_{\mathrm{B}} \langle T \rangle \gamma_D}{\rho_0^2} \operatorname{cth}^2 (k\delta_D) \right] \times$$
$$\times \left\{ \omega^2 \left(\frac{(\varkappa_0 + \varkappa_1) k}{k} + \frac{n (1 - m) \langle c \rangle (\varkappa_1 + \varkappa_0) \operatorname{th} (k\delta_D)}{D} + \rho_1 q \right)^2 + \right.$$
$$+ \frac{(\varkappa_1 + \varkappa_0) \Gamma k^3}{k} + (\varkappa_1 G_1 + \varkappa_0 G_0 + 2\varkappa n G_D) k +$$
$$\left. + \frac{\rho_1 q V^2}{2\chi_1} - \frac{nmV (\varkappa_1 + \varkappa_0) G_D \operatorname{th} (k\delta_D)}{D} \right\}^{-1}.$$

Here $G_{\mathbf{v}} = \left. \frac{d \langle T_{\mathrm{v}} \rangle}{dz} \right|_{z=\langle \varepsilon \rangle}$; $G_D = \left. \frac{d \langle c \rangle}{dz} \right|_{z=\langle \varepsilon \rangle}$; $\langle c \rangle = \langle c \rangle |_{z=\langle \varepsilon \rangle}$; $\langle T \rangle = \langle T_{\mathrm{v}} \rangle |_{z=\langle \varepsilon \rangle}$; $\varkappa = (\varkappa_0 + \varkappa_1)/2$

The characteristic times and scales of the fluctuation formations of the relief of the interphase boundary are determined by the position of the roots of the dispersion equation for the wave vectors in the complex half-plane:

$$\frac{2\varkappa \Gamma k^3}{k} + (\varkappa_0 G_0 + \varkappa_1 G_1 + 2n\varkappa G_D) k + \frac{\rho_1 q V^2}{2\chi_1} - \frac{2\varkappa nmVG_D \operatorname{th} (k\delta_D)}{D} = 0.$$

The characteristic scale of exponential cutoff of the correlation function $\langle \tilde{\varepsilon}(\mathbf{r}, t) \tilde{\varepsilon}(\mathbf{r}', t') \rangle$ is determined by the imaginary part of the root k_{Im}, while the characteristic scale of the spatially periodic part is given by its real part $2\pi k_{\mathrm{Re}}^{-1}$. The loss of morphological stability of the flat crystallization front is determined by the conditions of the process for which $k_{\mathrm{Re}} \sim 2\pi k_{\mathrm{Im}}$. Figure 2 shows the dependence of k_{Re} and k_{Im} on V for experiments under the conditions of microgravity (curves 1 and 2) and on earth (curves 3 and 4). It follows from them that as gravity becomes stronger the threshold growth velocities at which loss of morphological stability of the interphase boundary occurs increase. This qualitative dependence and the numerical values of the threshold velocities $V \cong 10^{-3}$ cm/sec are in agreement with the experimental data [4].

2. Generation of Acoustic Oscillations in the Temperature Gradient During Gaseous Epitaxy. A number of studies of thermal acoustic oscillations in pipes have been performed [7]. They were carried out neglecting friction in the gas for different models of heat transfer or using the boundary-layer approximation in describing the gas dynamics and heat transfer. In [8] the development of self-excited oscillations of the gas in a nonuniformly heated channel was studied from the viewpoint of the loss of stability of the stationary flow of gas taking into account the temperature dependence of the coefficients of viscosity and thermal conductivity.

We shall study the effect of white noise on locally equilibrium thermal fluctuations in the gas on the development of long-wavelength self-excited oscillations in a nonuniformly heated epitaxial reactor. It is assumed that the diameter of the reactor is much smaller than the length of the reactor, and therefore convective flows can be neglected. The system of nonstationary gas-dynamics and heat-conduction equations for a viscous ideal gas in the axisymmetric case has the form

$$\rho \frac{\partial \mathbf{v}}{\partial t} + \rho (\mathbf{v} \nabla) \mathbf{v} = -\operatorname{grad} p + \eta \Delta \mathbf{v} + \left(\frac{1}{3} \eta + \xi \right) \operatorname{grad} \operatorname{div} \mathbf{v} + \nabla \sigma^{\mathrm{st}}; \tag{2.1}$$

$$\frac{\partial \rho}{\partial t} + \operatorname{div} (\rho \mathbf{v}) = 0; \tag{2.2}$$

$$\rho c_p \left(\frac{\partial T}{\partial t} + (\mathbf{v} \nabla) T \right) = \varkappa \Delta T + \frac{\partial p}{\partial t} + (\mathbf{v} \nabla) p + \operatorname{div} \mathbf{q}_T^{\mathrm{st}}; \tag{2.3}$$

$$p = \rho B T. \tag{2.4}$$

Here ξ is the bulk viscosity of the gas and B is the specific gas constant of an ideal gas. To supplement (1.3), we write the correlation functions of the external stress tensor $\sigma_{ik}{}^{st}$, according to the fluctuation–dissipation theorem, as

$$\langle \sigma_{ij}^{\mathrm{st}}(\mathbf{r}, t)\,\sigma_{kl}^{\mathrm{st}}(\mathbf{r}', t')\rangle = 2k_{\mathrm{B}}\langle T\rangle \Big[\eta\,(\delta_{ik}\delta_{lj} + \delta_{il}\delta_{jk}) + \left(\xi - \frac{2}{3}\eta\right)\delta_{ij}\delta_{kl}\Big]\,\delta(\mathbf{r}-\mathbf{r}')\,\delta(t-t'). \tag{2.5}$$

We supplement Eqs. (2.1)-(2.5) and (1.3) with the boundary conditions

$$\mathbf{v}|_{r=R} = 0; \tag{2.6}$$

$$\left.\frac{\partial(\mathbf{v}\mathbf{n}_z)}{\partial \mathbf{r}}\right|_{r=0} = (\mathbf{v}\mathbf{n}_r)|_{r=0} = 0; \tag{2.7}$$

$$-\left.\frac{\partial T}{\partial r}\right|_{r=R} = \alpha\,(T|_{r=R} - T_{\mathrm{h}}), \tag{2.8}$$

where $\mathbf{n}_{r'}$, $\mathbf{n}_z$ are the orthonormal basis vectors of a cylindrical coordinate system.

Here it is assumed that the gas sticks to the walls of the reactor (2.6), the flow is axially symmetric (2.7), and Newton's law holds for heat transfer between the gas and the reactor (2.8). We denote by T_h the temperature at the heater, whose gradient is assumed to be constant and given. At the inlet ($z = 0$) and outlet ($z = \ell$) of the reactor soft boundary conditions hold:

$$\frac{\partial(\mathbf{v}\mathbf{n}_z)}{\partial \mathbf{z}} = \frac{\partial T}{\partial z} = \frac{\partial \rho}{\partial z} = 0. \tag{2.9}$$

Once again represent T, ρ, p, and $\mathbf{v}$ as sums of fluctuation and regular components. We integrate over the cross-section of the reactor the system of equations for $\tilde{T}$, ρ, $\tilde{p}$, and $\tilde{\mathbf{v}}$, linearized with respect to the fluctuations, from (2.1)-(2.4). Accordingly, we introduce new functions $\tilde{T}_s$, $\tilde{p}_s$, $\tilde{u}_s$, and $\tilde{\rho}_s$ sought, such that

$$\tilde{T}_s(z, t) = \frac{1}{\pi R^2}\int_0^R r\,dr \int_0^{2\pi} d\varphi\,\tilde{T}(r, z, \varphi, t),$$

$$\tilde{u}_s(z, t) = \frac{1}{\pi R^2}\int_0^R r\,dr \int_0^{2\pi} d\varphi\,\tilde{v}_z(r, z, \varphi, t)$$

($\tilde{v}_z$ is the component of the gas velocity $\tilde{\mathbf{v}}$ along the z axis).

In integrating the gradients of the velocities of the gas fluxes near the walls of the reactor it is assumed that the boundary layer approximation is valid:

$$\left.\frac{\partial v_z(r, z, t)}{\partial r}\right|_{r=R} \simeq -\frac{v_z(R-\delta_0, z, t)}{\delta_0}$$

(δ_0 is the thickness of the boundary layer). The value of δ_0 can be determined from the solution of the problem of the channel flow of incompressible viscous liquid oscillating with the frequency ω [5]:

$$\delta_0 = R/\mathrm{Re}\left(\frac{yJ_1(y)}{J_2(y)}\right), \quad y = \sqrt{-i\omega\eta/\langle\rho\rangle}. \tag{2.10}$$

Here J_1 and J_2 are Bessel functions of first and second orders, and $\langle\rho\rangle$ is the regular component of the density. In the case of a thin boundary layer

$$\delta_0 \simeq \frac{3}{2}\,\frac{\Gamma\left(\frac{3}{2}\right)}{\Gamma\left(\frac{5}{2}\right)}\,R\left(\sqrt{\frac{\omega\langle\rho\rangle}{2\eta}}\right)^{-1}$$

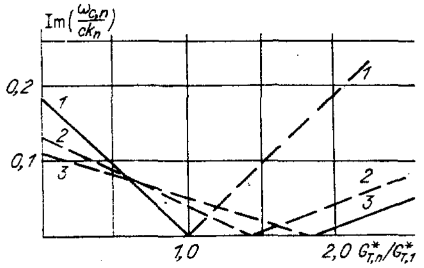

Fig. 3

(Γ is the gamma function). Finally we obtain the following system of equations for the fluctuation parts $\tilde{T}_s(z, t)$, $\tilde{u}_s(z, t)$, $\tilde{p}_s(z, t)$ and $\tilde{\rho}_s(z, t)$:

$$\langle p\rangle^{-1}\frac{\partial\tilde{p}_s}{\partial t}-\langle T\rangle^{-1}\frac{\partial\tilde{T}_s}{\partial t}+\frac{\partial\tilde{u}_s}{\partial z}=0; \tag{2.11}$$

$$\frac{\partial\tilde{u}_s}{\partial t}-\frac{1}{\langle\rho\rangle}\left(\frac{4}{3}\eta+\xi\right)\frac{\partial^2\tilde{u}_s}{\partial z^2}+\delta_s\tilde{u}_s=-\frac{c^2}{\gamma\langle\rho\rangle}\frac{\partial\tilde{p}_s}{\partial z}+(\nabla\sigma^{\mathrm{st}})_s; \tag{2.12}$$

$$\frac{\partial\tilde{T}_s}{\partial t}-\chi\frac{\partial^2\tilde{T}_s}{\partial z^2}+\alpha_s\tilde{T}_s=-G_T\tilde{u}_s+\frac{\gamma-1}{\gamma}\frac{\langle T\rangle}{\langle p\rangle}\frac{\partial\tilde{p}_s}{\partial t}+(\operatorname{div}\mathbf{q}_T^{\mathrm{st}})_s, \tag{2.13}$$

where γ is the adiabatic constant; $G_T = \partial\langle T\rangle/\partial z$ is the gradient of the regular component of the temperature field; $c = \sqrt{\gamma\langle p\rangle/\langle\rho\rangle}$ is the velocity of sound; and

$$\delta_s\simeq\frac{4}{3R^2\langle\rho\rangle}\left(\frac{4}{3}\eta+\xi\right)\frac{\Gamma\left(\frac{5}{2}\right)}{\Gamma\left(\frac{3}{2}\right)}\sqrt{\frac{\omega\langle\rho\rangle}{2\eta}};\quad\alpha_s=\frac{2\alpha\chi}{R}.$$

We are studying a nonuniformly heated reactor. Therefore the gas density $\langle\rho\rangle$ and temperature $\langle T\rangle$ and therefore the coefficients in the functions sought in (2.11)-(2.13) depend on z. To simplify the calculations we shall replace them by their average effective values, making the assumption that this will not affect the qualitative behavior of the functions so obtained. In addition, we set the temperature gradient G_T equal to a constant. Then the solution of (2.11)-(2.13) can be sought in the form

$$\tilde{u}_s=\sum_{n=0}^{\infty}\left[u_n\exp(ik_nz)+u_n^*\exp(-ik_nz)\right]$$

etc. Here $k_n = \pi n/\ell$ is the eigenvalue of the harmonic equation with homogeneous boundary conditions of the second kind at the boundary of the region (n = 0, 1, 2, ...). Fourier-transforming Eqs. (2.11)-(2.13) with respect to time, we can determine the spectral densities of the function sought $p_n(\omega)$, $u_n(\omega)$, $T_n(\omega)$ in terms of the functionals of the spectral densities of the random external forces. Using the fluctuation–dissipation theorem (1.3) and (2.5), for the spectral density of the correlation function of the pressure we obtain

$$\begin{aligned}\langle\tilde{p}_n^2\rangle_{k_n,\omega}=&\left\{\frac{2k_B\varkappa}{\pi}\left(\frac{\gamma-1}{\gamma}\right)^2\omega^2\left[\omega^2+\left(\frac{k_n^2}{\langle\rho\rangle}\left(\frac{4}{3}\eta+\xi\right)+\delta_s^n\right)^2\right]-\right.\\&\left.-k_n^2\frac{k_B\langle T\rangle}{\pi}\left(\frac{4}{3}\eta+\xi\right)\frac{c^2}{\gamma}\left[\omega^2+\left(k_n^2\chi+\alpha_s+\frac{G_T}{\langle T\rangle}\frac{\omega}{k_n}\right)^2\right]\right\}\times\\&\times\left\{\frac{\omega}{k_n^2\gamma^2}\left[-\omega^2+k_n^2c^2+\gamma\left(\frac{k_n^2}{\langle\rho\rangle}\left(\frac{4}{3}\eta+\xi\right)+\delta_s^n\right)(\chi k_n^2+\alpha_s)\right]^2+\right.\\&\left.+\left[\frac{1}{k_n}\left(k_n^2c^2(k_n^2\chi+\alpha_s)-\omega^2\left(\frac{k_n^2}{\langle\rho\rangle}\left(\frac{4}{3}\eta+\xi\right)+\chi k_n^2+\alpha_s+\delta_s\right)\right)+\omega\frac{G_T}{\langle T\rangle}c^2\right]^2\right\}^{-1}.\end{aligned} \tag{2.14}$$

The characteristic fluctuation times of the harmonics with wave vector k_n are determined by the roots of the dispersion equation

$$\frac{\omega}{\gamma k_n}\left\{-\omega^2+k_n^2c^2+\gamma\left[\frac{k_n^2}{\langle\rho\rangle}\left(\frac{4}{3}\eta+\xi\right)+\delta_s^n\right](\chi k_n^2+\alpha_s)\right\}-\frac{1}{ik_n}\times$$
$$\times\left\{k_n^2(k_n^2\chi+\alpha_s)c^2-\omega^2\left[\frac{k_n^2}{\langle\rho\rangle}\left(\frac{4}{3}\eta+\xi\right)+\chi k_n^2+\alpha_s+\delta_s^n\right]\right\}+i\omega\frac{G_Tc^2}{\langle T\rangle}=0 \tag{2.15}$$

in the complex frequency plane ω. Here $\delta_s^n=\delta_s|_{\omega=ck_n}$. In the general case, all roots of (2.15) are complex. There exist, however, critical values of the temperature gradient G_T^* for which real roots of the dispersion equation exist. Figure 3 shows the dependence of the imaginary part $\operatorname{Im}\omega_{c,n}$ of the root of (2.15) normalized to the velocity of sound in the gas c and the wave number k_n, on the temperature gradient in the gas, scaled to the critical gradient $G_{t,1}^*$ of the first harmonic.

Results were obtained for the first, second, and third harmonics of a quartz reactor (curves 1-3) with argon as the carrier gas. The real part of the root $\operatorname{Re}(\omega_{c,n}) \simeq ck_n$ with good accuracy. The reactor is 50 cm long and 5 cm in diameter. For a heater temperature of ≈870°K and a pressure of $\sim 10^5$ Pa in the reactor the critical magnitude of the temperature gradient for the first harmonic $G_{T,1}^* \sim$ 3000-4000 deg/m. Thus, when $G_T = G_{T,n}^*$, where

$$G_{T,n}^*=\frac{\langle T\rangle}{c}\left[\frac{k_n^2}{\langle\rho\rangle}\left(\frac{4}{3}\eta+\xi\right)+\delta_s^n+(\gamma-1)(\chi k_n^2+\alpha_s)\right],$$

there exists a real root of (2.15), corresponding to the frequency of the acoustic wave of the harmonic k_n of the reactor: $\omega_{c,n}^* \simeq ck_n$. In the region of temperature gradients close to critical gradients, the correlation function of the pressure fluctuations

$$\langle\tilde p_s(z,t),\tilde p_s(z',t')\rangle\simeq\frac{\exp\left(-\frac{t-t'}{\psi^n}\right)}{|G_T-G_{T,n}^*|}\times$$
$$\times\operatorname{Re}\left[p_{G,n}^2\exp\left(ik_n|z-z'|+i\omega_{c,n}|t-t'|\right)\right], \tag{2.16}$$

where $\psi^n=\dfrac{\psi_0^n}{|G_T-G_{T,n}^*|}$; $\psi_0^n=(\varepsilon_0^n\sin(\varphi_n))^{-1}$;

$$p_{G,n}^2=\left[\frac{2k_B\varkappa}{\pi}\left(\frac{\gamma-1}{\gamma}\right)^2(k_n^2c^2+2k_nc\varepsilon^*|G_T-G_{T,n}^*|)^2\times\right.$$
$$\times\left(k_n^2c^2+2ck_n\varepsilon^*|G_T-G_{T,n}^*|+\left(\left(\frac{4}{3}\eta+\xi\right)\frac{k_n^2}{\langle\rho\rangle}+\delta_s^n\right)^2\right)-$$
$$-\frac{k_B\langle T\rangle k_n^2c}{\pi\gamma}\left(\frac{4}{3}\eta+\xi\right)\left(k_n^2c^2+2ck_n\varepsilon^*|G_T-G_{T,n}^*|+\right.$$
$$\left.\left.+\frac{G_T}{\langle T\rangle c}+\left(\frac{1}{c}-\frac{G_T\varepsilon^*}{\langle T\rangle k_n}\right)|G_T-G_{T,n}^*|+k_n^2\chi+\alpha_s^n\right)^2\right)\right]\times$$
$$\times\left\{\frac{-2k_nc^4\langle T\rangle}{\gamma^2}\left((\gamma+1)(k_n^2\chi+\alpha_s)+\gamma\left(\left(\frac{4}{3}\eta+\xi\right)\frac{k_n^2}{\langle\rho\rangle}+\delta_s^n\right)\right)+\right.$$
$$\left.+2\varepsilon^*\left(4k_n^2c^4\gamma^2+c^2\left(\left(\frac{4}{3}\eta+\xi\right)\frac{k_n^2}{\langle\rho\rangle}+\delta_s^n+\chi k_n^2+\alpha_s\right)+\sqrt{\gamma}(\chi k_n^2+\alpha_s)\right)^2\right\}^{-1};$$

$$\varepsilon^*=\varepsilon_0^n\exp(i\varphi_n);\ \varepsilon_0^n=2k_n^2c^6\left\{4k_n^2c^4\gamma^2+c^2\left(\left(\frac{4}{3}\eta+\xi\right)\frac{k_n^2}{\langle\rho\rangle}+\right.\right.$$
$$\left.\left.+\delta_s^n+\chi k_n^2+\alpha_s\right)+\sqrt{\gamma}(\chi k_n^2+\alpha_s)\right)^2\right\}^{-1};$$

$$\varphi_n=\operatorname{arctg}\left(\frac{\sqrt{\varepsilon_0^n-g_n^2}}{g_n}\right);\quad g_n=-\frac{2k_nc^4\langle T\rangle}{\gamma^2}\Big((\gamma+1)(k_n^2\chi+\alpha_s)+$$

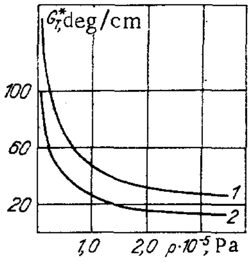

Fig. 4

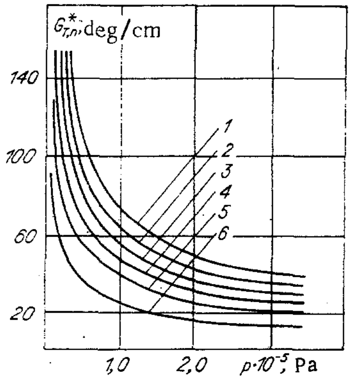

Fig. 5

$$+\gamma\left(\left(\frac{4}{3}\eta+\xi\right)\frac{k_n^2}{\langle\rho\rangle}+\delta_s^n\right)\Bigg)\left\{4k_n^2c^4\gamma^2+c^2\left(\left(\left(\frac{4}{3}\eta+\xi\right)\frac{k_n^2}{\langle\rho\rangle}+\right.\right.\right.$$

$$\left.\left.\left.+\delta_s^n+\chi k_n^2+\alpha_s\right)+\sqrt{\gamma}\left(\chi k_n^2+\alpha_s\right)\right)^2\right\}^{-1}.$$

In (2.16) ψ^n is the characteristic correlation time, while $\omega_{c,n}$ is the characteristic frequency of the long-wavelength part of the pressure fluctuations:

$$\omega_{c,n}=ck_n+\varepsilon_0^n\cos(\varphi_n)\left(G_T-G_{T,n}^*\right). \tag{2.17}$$

As one can see from (2.16), the amplitude of the pressure fluctuations increases as $|G_T - G_{T,n}^*|$ decreases. The correlation time ψ^n exhibits an analogous dependence. At the same time the n-th harmonic of the reactor is separated and an acoustic wave with frequency $\omega_{c,n}{}^*$ is generated. We note that the estimates (2.16) and (2.17) are valid for values of G_T close to $G_{T,n}{}^*$, where the nonlinear effects of the interaction of fluctuations are still insignificant.

Figure 4 shows the dependence of the magnitude of the critical gradient $G_{T,1}{}^*$ for the first harmonic on the pressure and temperature. The results were obtained for two limiting values of the coefficient of thermal conductivity $\alpha = \infty$ and 0 (curves 1 and 2) for the same parameters of the gas in the reactor as in Fig. 3. It follows from them that when α decreases $G_{T,n}^*$ decreases. Figure 5 shows the dependence of $G_{T,n}^*$ on the pressure for $\alpha = 0$ for different harmonics (n = 1, ..., 6 – curves 6-1); one can see that $G_{T,n}^*$ increases as n increases. These results agree qualitatively with the data from gas-dynamic experiments on the study of mechanisms of thermoacoustic oscillations in application to the explanation of oscillatory combustion effects [7, 8].

Thus the approach developed, based on the determination of the effect of white noise of thermal fluctuations, is effective for studying the kinetics of threshold processes for a wide class of phenomena in open statistical systems. It was shown that fluctuations can lead to the formation of stationary and nonstationary periodic structures. In application to crystallization processes they could be responsible for the appearance of periodic nonuniformities in the distribution of impurities and defects in the solid phase formed for values of the technological parameters of the process close to critical values.

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