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MATHEMATICAL MODELING OF THE DYNAMICS OF NONEQUILIBRIUM CRYSTALLIZATION FROM A SUPERSATURATED SOLUTION

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Based on a qualitative and numerical analysis of the stability of dynamic regimes of the crystallization process in a metastable solution-crystal system, resonance conditions are investigated in the case of periodic external disturbances of the temperature of the medium.

The formation the structure of a substance during crystallization from a solution under metastable conditions depends on both the process conditions and the kinetics of phase transformation [1-4]. Solid phase growth often proceeds in a vibrational mode [5-7], which is one of the reasons for a laminated structure in crystals. Moreover, such phase transformation may take place in the combined processes of monomer polymerization and polymer crystallization [8, 9]. Theoretical studies of nonequilibrium phase transformations on the macrokinetic level are important because of the need to control these phenomena in process installation.

The goal of the present work is to study the stability of possible stationary regimes of nonequilibrium crystallization in a homogeneous solution-crystal system and to analyze the possible response of the system to an external periodic disturbance.

We will consider a nonstationary process of crystal growth from a single solution in a cylindrical crystallizer with semipermeable walls. Supersaturation X_w is maintained on the crystallizer walls at the temperature T_w. It is assumed that the growth of a new phase proceeds in the bulk at a finite rate and depends on the temperature according to the Arrhenius law [10, 11]:

$$\frac{dX}{dt} = (X - X_0)\, K \exp\left(-\frac{E}{RT} \right).$$

Analogously, the growth rate of crystals in a single-substance solution with a small concentration of impurity is described. For instance, in [11], the effect of raffinose on the growth rate of saccharose crystals is investigated.

The temperature dependence of substance solubility is taken into account according to the exponential law [1, 2]

$$X_0 = K_1 \exp\left(-\frac{E_1}{RT} \right).$$

It is assumed that the thermophysical characteristics of the solution are constant.

A macrokinetic one-dimensional model is represented by a system of diffusion equations for the solute concentration and the thermal conductivity. In terms of dimensionless variables we have

$$\frac{\partial Y}{\partial \tau} = \mathrm{Le} \left(\frac{\partial^2 Y}{\partial s^2} + \frac{1}{s} \frac{\partial Y}{\partial s} \right) - w; \tag{1}$$

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$$\frac{\partial\Theta}{\partial\tau} = \frac{\partial^2\Theta}{\partial s^2} + \frac{1}{s}\frac{\partial\Theta}{\partial s} + qw ;$$

$$\tau = 0 : \quad Y = Y_{\text{in}} ; \quad \Theta = \Theta_{\text{in}} ; \tag{2}$$

$$\tau > 0 \begin{cases} s = 0 : & \dfrac{\partial Y}{\partial s} = 0 ; \quad \dfrac{\partial\Theta}{\partial s} = 0 ; \\ s = 1 : & T = Y_{\text{w}} , \quad \Theta = \Theta_{\text{w}} . \end{cases} \tag{3}$$

Here

$$w = \left[Y - k_1 \exp\left(- \frac{U}{\Theta} \right) \right] k \exp\left(- \frac{1}{\Theta} \right) \tag{4}$$

is the growth rate of crystals;

$$\Theta = \frac{R}{E} T , \quad Y = \frac{X}{X_{\max}} , \quad \tau = \frac{at}{r_0^2} , \quad s = \frac{r}{r_0}$$

are the temperature, concentration, time, and coordinate, respectively;

$$\text{Le} = \frac{D}{a} , \quad q = \frac{RLX_{\max}}{\rho cE} ; \quad U = \frac{E_1}{E} ; \quad k = \frac{Kr_0^2}{a} ; \quad k_1 = \frac{K_1}{X_{\max}}$$

are the Lewis number, heat of phase transformation, activation energy, frequency factor, and solubility parameter, respectively; $X_{\max}$ is the solute concentration at the limiting supersaturation required for the onset of crystallization. It is assumed that $X_{\text{w}} \leq X_{\max}$.

The presence of nonlinear sources in (1)-(4) makes the crystallization dynamics intricate. Therefore, problem (1)-(4) is first simplified from a spatial to a zero-dimensional dynamic problem [12, 13]. To investigate the stability of possible stationary states of the simplified dynamic system, the first Lyapunov method is used [14]. Then, using the results of the zero-dimensional approximation, the stability of stationary regimes of the spatial problem is studied numerically. Many authors use this approach for qualitative analysis of solutions of distributed problems [15-19], which allows design of a numerical experiment aimed at determining the unstable states of model (1)-(4).

Changing from distributed equations (1)-(3) to equations with lumped parameters is performed by approximating the spatial derivatives in Eqs. (1) by finite-difference analogs. The continuous set of points of the spatial coordinate on the segment [0, 1] is replaced by a discrete set consisting of three points, namely, the two boundary points, at which functions are prescribed by boundary conditions, and the central point, at which the functions are unknown. Thus, problem (1)-(4) is reduced to a dynamic system the number of whose equations is equal to the number of unknown functions [12].

The zero-dimensional model produced by such a transformation is described by the system of two ordinary differential equations

$$\frac{dY}{\partial\tau} = 6 \, \text{Le} \, (Y - Y_{\text{w}}) - w \equiv P_1 (Y , \Theta) ;$$

$$\frac{d\Theta}{d\tau} = 6 (\Theta_{\text{w}} - \Theta) + qw \equiv P_2 (Y , \Theta) ; \quad \tau = 0 : \quad Y = Y_{\text{in}} , \quad \Theta = \Theta_{\text{in}} . \tag{5}$$

The stability of solutions of system (5) is investigated in two stages. First, the possibility of the existence of nonunique stationary regimes and, second, the stability of the determined unique and multiple steady states (equilibrium states) are investigated.

The coordinates of the parametric space of nonunique regimes of the zero-dimensional model are determined from the nonlinear algebraic equations

$$P_i\,(Y_{\mathrm{s}}\,,\ \Theta_{\mathrm{s}}) = 0\,, \quad i = 1\,,\ 2\,, \tag{6}$$

by the bifurcation diagram method [20]. If we eliminate Y_{s} from Eqs. (6) and solve them for one of the parameters, e.g., Y_{w}, then we obtain the equations of a bifurcation curve in the following form:

$$Y_{\mathrm{w}} = \frac{\Theta_{\mathrm{s}} - \Theta_{\mathrm{w}}}{q}\left[\frac{6}{k\exp\left(-\dfrac{1}{\Theta_{\mathrm{s}}}\right)} + \frac{1}{\mathrm{Le}}\right] + k_1\exp\left(-\frac{U}{\Theta_{\mathrm{s}}}\right). \tag{7}$$

Expression (7) relates the coordinates of the stationary states Θ_{s} to the concentration Y_{w}. As is seen from (7), Y_{w} changes nonlinearly with Θ_{s}, and in the certain range of Y_{w} the dynamic system (5) has three stationary states. The bounds of Y_{w} at which nonunique states are possible are determined from the extreme points of bifurcation diagram (7). On this basis, a second equation for determination of the bounds of multiple regimes in the parametric plane may be derived. For this, the right-hand side of (7) is differentiated with respect to Θ_{s} and equated to zero. The equality obtained is solved for the parameter q:

$$q = \frac{1}{U k_1\exp\left(-\dfrac{U}{\Theta_{\mathrm{s}}}\right)}\left[\frac{6\,(\Theta_{\mathrm{s}} - \Theta_{\mathrm{w}} - \Theta_{\mathrm{s}}^2)}{k\exp\left(-\dfrac{1}{\Theta_{\mathrm{s}}}\right)} - \frac{\Theta_{\mathrm{s}}^2}{\mathrm{Le}}\right]. \tag{8}$$

Parametric equations (7) and (8) determine the domains of q and Y_{w} in which a nonequilibrium crystallization process in the system under consideration may proceed in the regime of multiple stationary states. For concrete values of the other parameters in Eqs. (7) and (8) the ranges of q and Y_{w} are calculated in which the zero-dimensional problem has multiple stationary solutions.

Figure 1a shows nonuniqueness domains (solid line) in the q, Y_{w} plane for two values of k. For parameter values in the region of wedge I, three stationary states may exist: low-temperature, moderate-temperature, and high-temperature states. The moderate-temperature state is unstable.The process for upper or lower states is determined by the initial state of the system. For parameter values outside region I only a unique stationary state is realized. In region II, this state is low-temperature, while in region III this state is high-temperature.

The position and dimensions of the nonuniqueness domains are determined by the conditions for conducting the process and its kinetics. With increasing parameter k, the nonuniqueness bounds are shifted toward lower q and higher Y_{w} values. It may be said that with increasing reactor size r_0, the multiple regimes can occur at lower concentrations for solution supersaturation $X_{\max}$.

The stability of possible stationary states of simplified problem (5) is studied by a perturbation method [14]. The coefficients of the characteristic (quadratic) equation of the linearized model are of the form

$$\Delta = (P_1)'_Y\,(P_2)'_\Theta - (P_1)'_\Theta\,(P_2)'_Y\,; \tag{9}$$

$$\sigma = -\,(P_1)'_Y - (P_2)'_\Theta\,. \tag{10}$$

The equilibrium state is stable if the real parts of the roots of the characteristic equation are positive. Then from the Routh-Hurwitz conditions or a direct analysis of the roots of the characteristic equation it follows that for the equilibrium state to be stable, the coefficients of (9), (10) must be positive. Parametric equations of the boundaries of possible positions of equilibrium are determined from equality of coefficients (9) and (10) to zero. Equations of

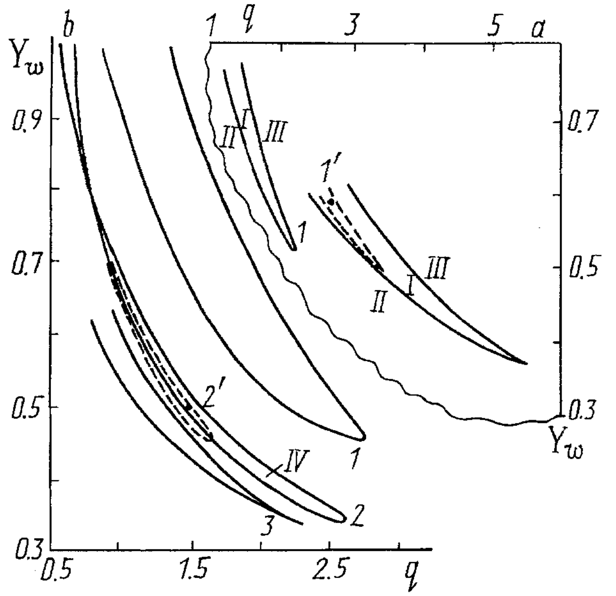

Fig. 1. Domains of nonuniqueness (a) and instability (b), $U = 0.5$; $\ln k_1 = 7$, $\Theta_w = 0.05$; solid lines, zero-dimensional model; dashed lines, one-dimensional model: a) $\mathrm{Le} = 0.03$; $\ln k = 15$ (1), 14.5 (2); b) $\ln k = 15.5$; $\mathrm{Le} = 0.01$ (1); 0.04 (2); 0.1 (3); 1' and 2', parametric variants for Figs. 2, 3.

the boundary of saddle-type instability are specified by expressions (6) and $\Delta = 0$. For problem (5), the parametric equations of the saddle boundaries and the multiple stationary states coincide. Then the mean unstable state is a saddle ($\Delta < 0$).

Expressions (6) and $\sigma = 0$ determine the limits of stability of the positions of equilibrium "focus and node"; at $\sigma < 0$ they are unstable. One of the parametric equations is specified by expression (7) for Y_w, and the other has the form

$$q = \frac{1}{U k_1 \exp\left(-\frac{U}{\Theta_s}\right)} \left[\frac{6\,[\Theta_s - \Theta_w - \Theta_s(\mathrm{Le} + 1)]}{k \exp\left(-\frac{1}{\Theta_s}\right)} - \Theta_s^2 \right]. \qquad (11)$$

Figure 1b shows the instability limits (solid line) calculated by Eqs. (7), (11) at different Le values. Closed region IV corresponds to unstable equilibrium positions. For the parameters q, Y_w of this region self-oscillations may develop in the solution-crystal system. Instability region IV exists only for a certain Le range. With increasing or decreasing Le number, only the saddle-type instability is manifested. For q, Y_w values outside region IV, the equilibrium positions are stable.

The position and dimensions of the instability regions also depend on the process conditions and its kinetics. Substances with lower activation energy of self-diffusion are characterized by a large instability region, with the instability boundaries being displaced toward smaller Y_w and larger q. With increasing reactor radius, the region of self-oscillations increases as well but only with a shift in the opposite direction.

Relations (6) and $\sigma^2 - 4\Delta = 0$ determine an interface between foci ($\sigma^2 - 4\Delta < 0$) and nodes ($\sigma^2 - 4\Delta > 0$). Parametric equations determining this interface are described by (7) for Y_w and a quadratic equation for q (not given because of its bulky form). Thus, we have two pairs of equations for the focus-node interface that specify the domains of existence of these equilibrium positions.

Results of an approximate qualitative analysis of the stability of the stationary states of problem (5) have been confirmed by its numerical solution. System (5) is nonlinear; it was solved by tested numerical methods [21]. A numerical experiment showed that the nonuniqueness boundaries determined theoretically by formulas (7), (8) and numerically, in fact, coincide.

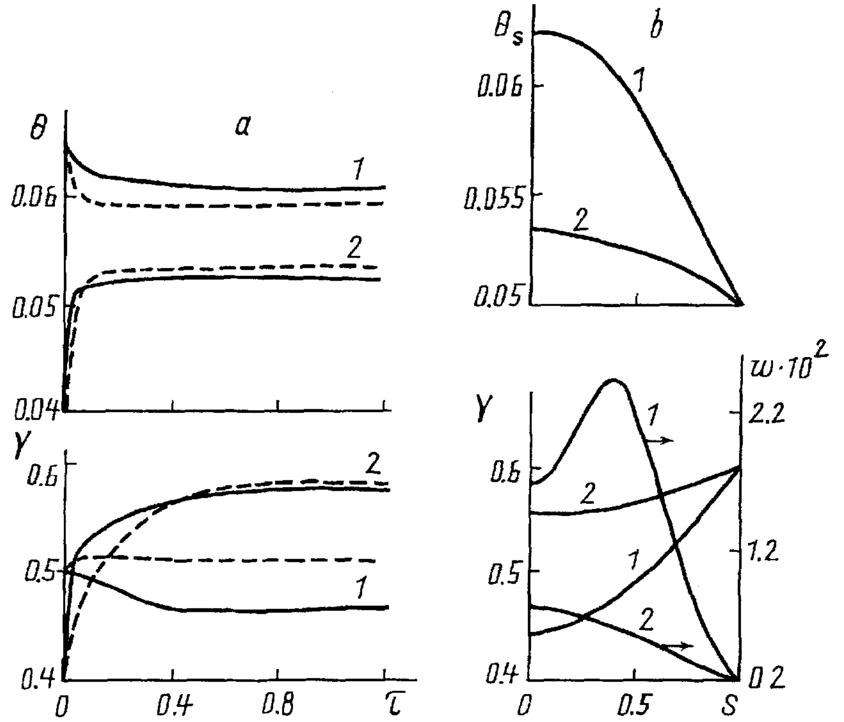

Fig. 2. Multiple regimes, $Y_w = 0.6$; $q = 2.7$ (variant 1′ in Fig. 1a): a) time variation of functions for the zero-dimensional (solid line) and one-dimensional (dashed lines) models; b) stationary profiles of high-temperature (1) and low-temperature (2) regimes.

Figure 2 (solid line) presents results of a numerical solution in the case of multiple stationary states for the parameters of point 1′ in Fig. 1a. Depending on the initial state of the system, the crystallization process proceeds in either a high-temperature (line 1) or a low-temperature (line 2) regime. Temperature values in the lower $\Theta_{s\,\text{low}}$ and upper $\Theta_{s\,\text{up}}$ stationary regimes, determined from both (6) and (5), coincide up to the third decimal place and are as follows: $\Theta_{s\,\text{low}} = 0.052$; $\Theta_{s\,\text{up}} = 0.061$.

The high-temperature regime is characterized, as compared to the low-temperature one, by strong supercooling ($\Theta_{s\,\text{low}} - \Theta_w < \Theta_{s\,\text{up}} - \Theta_w$) and a high crystallization rate ($w_{s\,\text{low}} = 0.004$; $w_{s\,\text{up}} = 0.024$). These results agree with the experimental data in [1, 2], which show a considerable increase in crystal growth rate with increase in temperature. Thus, by regulating the initial conditions of crystal growth, one may control the crystallization process.

Results obtained for the nonunique stationary states of zero-dimensional simplified model (5) were used as a basis in a numerical experiment concerned with determination of multiple and self-oscillation regimes of one-dimensional problem (1)-(4). This problem was solved by a finite-difference method according to a conventionally stable explicit scheme [21]. In each time layer the time step was corrected proceeding from the stability condition for Eqs. (1).

The nonuniqueness boundaries obtained for the one-dimensional problem are represented by a dashed line in Fig. 1a. The nonuniqueness region of the one-dimensional model is smaller than that of the zero-dimensional model (the solid line). The results of an approximate analytical investigation and numerical solutions of both models for parameters values inside the "dashed" wedge are in both qualitative and quantitative agreement. Thus, the dashed line in Fig. 2a shows the numerical solution of problem (1)-(4) for variant 1′ of Fig. 1a for values of the temperature Θ_{av} and concentration Y_{av} averaged over the crystallizer radius. Stationary values of layer-averaged temperatures in the lower and upper regimes are as follows: $\Theta_{av\,\text{low}} = 0.053$ and $\Theta_{av\,\text{up}} = 0.059$.

Figure 2b shows stationary profiles of the temperature, concentration, and growth rate of crystals for the high-temperature (line 1) and low-temperature (line 2) regimes. Nonlinearity of the process in a metastable

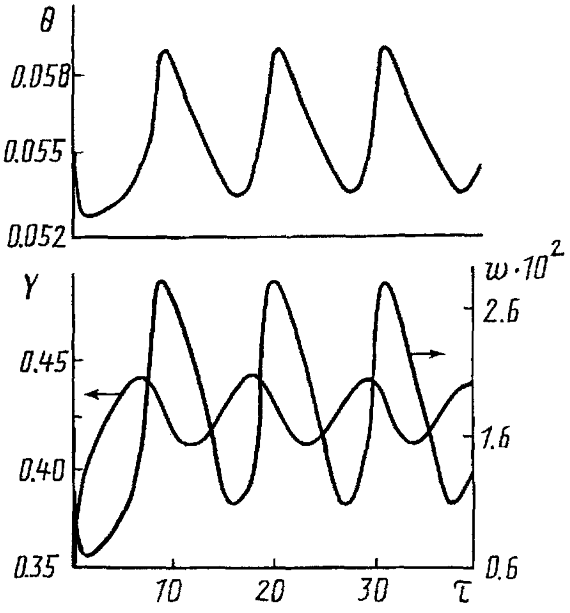

Fig. 3. Self-oscillations for the one-dimensional model, $Y_w = 0.5$; $q = 1.48$ (variant 2′ in Fig. 1b).

solution-crystal system is manifested in the formation of spatial structures. In the low-temperature regime, crystallization proceeds, in fact, in the bulk and at a lower rate of phase transformation than in the upper one. In the high-temperature regime, a crystallization front is established in the middle part between the axis and the walls.

A numerical study of the self-oscillation regimes of the one-dimensional problem revealed that processes of diffusion of a substance and heat exert a stabilizing effect on nonequilibrium crystallization since the instability region of the oscillatory solutions of the one-dimensional model (Fig. 1b, the dashed line), just as for the nonunique solutions, is smaller than the corresponding region of the zero-dimensional model.

An example of the self-oscillations obtained is given in Fig. 3 for the parameters of point 2′ in Fig. 1b. The period of these oscillations $T_z \approx 11$ agrees with that calculated in a qualitative linear analysis of the zero-dimensional model using the formula

$$T_l = 2\pi \,/\, \sqrt{\sigma^2 - 4\Delta} \approx 8 \,.$$

The stationary values of the temperature, concentration, and growth rate of crystals for this variant determined by the bifurcation diagram method are as follows: $\Theta_s = 0.0535$; $Y_s = 0.441$; $w_s = 0.0142$. The nonlinear dependence of the solubility and the rate of phase transformation on the temperature influences the mode of oscillations. Evolution of the concentration proceeds, in fact, according to a harmonic law. Oscillations of the temperature and the growth rate have a distorted symmetry. The difference of the oscillation phase of the solution concentration from that of the temperature and the transformation rate is attributed to different rates of supply and removal of heat and the substance as well as to the kinetics of phase transformation. It may be said that the minimum oscillations pertain to the low-temperature state, and the maximum ones pertain to the high-temperature state. Oscillatory regimes in crystallization are probably one of the reasons for forming substances with a periodic structure.

Thus, it may be concluded that the zero-dimensional lumped model reflects the dynamics of one-dimensional distributed model (1)-(4) qualitatively and, to a permissible accuracy, quantitatively. Therefore, simplified model (5) has been used to investigate the response of the considered solution-crystal system to periodic disturbances in the external medium. It is assumed that the temperature Θ_w changes in time according to the harmonic law

$$\Theta_w = A_w + A_d \cos(\omega \tau) \,. \tag{12}$$

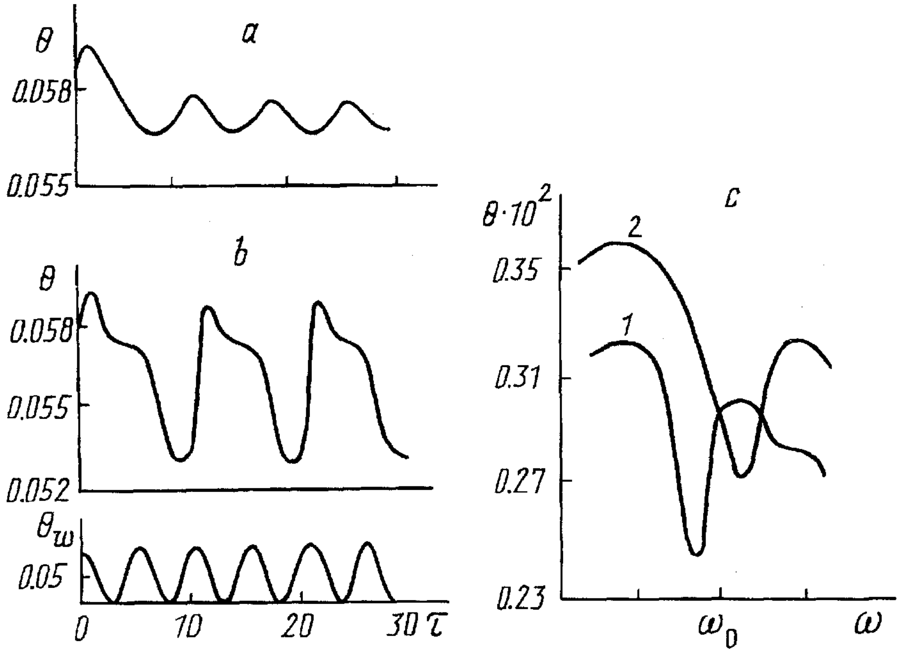

Fig. 4. Oscillations for the zero-dimensional model, Le = 0.03; ln k = 15.5; Y_w = 0.4; q = 2.84; a) damping oscillations (without disturbance); b) forced oscillations for a disturbance with the frequency $\omega = 3/2\omega_0$; c) amplitude-frequency characteristics, A_d/A_w = 0.002 (1); 0.004 (2).

Resonance characteristics have been investigated for the stationary regime with slowly damping oscillations of undisturbed system (5), whose dynamics is shown in Fig. 4a. The responses of system (5) to periodic disturbance (12) have been studied for two disturbance amplitudes, namely, $A_d/A_w = 0.002$ and $A_d/A_w = 0.004$ with $A_w = 0.05$. Figure 4c shows amplitude-frequency characteristics (curves 1 and 2 respectively) obtained from numerical calculations. Here, the oscillation amplitude is the difference between the maximum and minimum temperatures with oscillations. An increase in the disturbance amplitude A_d causes an increase in the amplitude of forced oscillations and, consequently, it changes the character of the frequency-amplitude curves: the number of resonance peaks decreases, their region broadens, and no resonance is observed at the natural frequency ω_0. At a smaller disturbance amplitude resonance phenomena are observed near the natural frequency ω_0 and at the multiple values $2/3\omega_0$ and $3/2\omega_0$ of it.

The results obtained indicate nonlinearity of the resonance phenomena in the nonequilibrium crystallization process under consideration. This is also confirmed by a change in the character of forced oscillations with increase in the frequency of the external disturbance.

We now consider the evolution of the amplitude of forced oscillations as a function of the disturbance frequency for $A_d/A_w = 0.002$. At disturbance frequencies near the natural one and smaller than ω_0 the periods of the disturbing and forced oscillations increase. As the frequency ω increases, the dynamics of the resultant oscillations changes qualitatively. For a disturbance frequency near ω_0, the resonance oscillations have two peaks. When the disturbance frequencies exceed ω_0, the two-peak character is more distinct and it may be said that the forced oscillations occur with a period that is twice that of the disturbing oscillations. With a further increase in the disturbance frequency, the two peaks flatten, and the oscillations become more monotonic. In this case, the response oscillations occur with a doubled period. Such oscillations are illustrated in Fig. 4b. The lower graph shows periodic disturbance (12), and the upper graph is the temperature response of the solution-crystal system to this disturbance.

The proposed model of nonequilibrium single-solution crystallization (1)-(4) makes it possible to study nonlinear effects related to the kinetics of the process, predict formation of the structure of solids, and control preparation of substances with desired properties.

NOTATION

a, D, thermal diffusivity and diffusion coefficient, respectively; c, specific heat; E, E_1, activation energy of solute self-diffusion and dissolution, respectively; K, K_1, preexponential factor of self-diffusion and dissolution, respectively; K_g, growth rate constant; L, heat of crystallization; r, coordinate; r_0, reactor radius; R, universal gas constant; t, time; T, temperature; T_z, T_l, oscillation period; w, crystal growth rate; X, solution concentration; ρ, density; ω, frequency. Subscripts: 0, saturation or eigenvalue; d, disturbance; w, reactor wall; max, maximum possible; in, initial; s, steady state.

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