

## STABILITY ANALYSIS OF THE GROWTH OF PARTICLES OF A POLYDISPERSE SYSTEM IN A SOLUTION UNDER NONISOTHERMAL CONDITIONS

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*A mathematical model of continuous saline crystallization from solutions based on the crystal-size distribution function is considered. A steady solution is obtained and its stability is studied.*

**Introduction.** In determining the basic parameters of the growth of a polydisperse particle system in a solution with some particles removed from the system and new particles formed, one can observe the loss of stability of the steady solution for the system and origination of self-induced oscillations in a certain range of parameters [1, 2]. The main problems that are of interest for practical application of this process are to determine this domain and its “deformations” taking into account new characteristics, to find the frequencies of oscillations that appear in the soft regime of instability, and to determine the parameters that characterize the system of particles when it loses stability. Similar problems arise in studying the evolution of a polydisperse system of bubbles [3]. In both cases, the equation for the particle(bubble)-size distribution function appears, and the mass-transfer equation for the dissolved substance is replaced by the heat-transfer equation. In this case, the “motive force” of the process is the difference in the current and equilibrium temperatures (overheating) rather than the difference in the corresponding concentrations (oversaturation of the solution).

At present, the main focus in studies of the crystallization process is on the effect of mass-transfer phenomena on the stability characteristics of a system of solid particles (crystals) growing in an oversaturated solution [1, 2]. In this case, it is assumed that the process is isothermal, while it is known that energy is released (spent) in the process of crystallization, and this, in a number of cases, substantially affects the characteristics of the process [4–6].

The mathematical model of the process includes a system of three nonlinear differential equations (two ordinary differential equations and one partial differential equation), which has no analytical solution in the general case. The situation becomes simpler in the steady case, where the problem can be reduced to nonlinear transcendental equations. In this case, the problem of stability analysis of the steady solution arises.

The characteristic feature of stability problems for steady solutions of equations of continuous mass crystallization is that the characteristics of the loss of stability (frequencies of arising self-induced oscillations, growth rate of an unstable mode that appears when the solution loses stability, etc.) depend on many dimensionless parameters. We note that some variables weakly affecting the steady solution may considerably change the characteristics of the loss of stability, because the corresponding equations contain derivatives of these variables, which need not be small.

According to the above arguments, it is very promising to develop a general method for obtaining equations for the characteristics of the loss of stability (mainly, manifolds of appropriate dimensions that separate domains of stability of the steady solution from domains of instability) and for subsequent analysis

of the equations obtained. We will also take into account the effect of heat released from solutions in the crystallization process on the stability characteristics of the system.

**1. Formulation of the Problem.** In formulating the basic equations of the problem, we ignore fluctuations of the crystal growth rate and the effects of aggregation and cleavage of the crystals. We assume that the suspension in the system is perfectly mixed. With these assumptions, the basic system of equations of continuous mass crystallization can be written as

$$\frac{\partial f}{\partial t} + V(C, T) \frac{\partial(r^{1-\alpha} f)}{\partial r} = \frac{f_* - f}{\tau}; \quad (1.1)$$

$$\frac{dC}{dt} = Q(C) - \rho V(C, T) \int_0^\infty r^{3-\alpha} f(r, t) dr; \quad (1.2)$$

$$\frac{dT}{dt} = W(C, T) + lV(C, T) \int_0^\infty r^{3-\alpha} f(r, t) dr. \quad (1.3)$$

Equation (1.1) expresses the material balance of the principal component in the solid phase. Here  $f$  is the crystal-size distribution function,  $C$  is the concentration of the principal component in the solution,  $T$  is the temperature,  $r$  is the crystal radius,  $t$  is the time,  $\tau$  is the time of particle transportation through the system, and  $f_*$  is the distribution function at the entrance to the crystallizer, which may be equal to zero in real situations, describe the fraction of crystals during recrystallization, etc. We assume that  $f_*$  is a function of the crystal size  $r$  only. The function  $V(C, T)$  is related to the accepted law of crystal growth

$$\frac{dr}{dt} = V(C, T)r^{1-\alpha}. \quad (1.4)$$

Usually, this function is taken in the form

$$V(C, T) = a(T)[C - C_0(T)]^k \quad (k = \text{const}), \quad (1.5)$$

where the difference  $C - C_0(T)$  is the oversaturation of the solution,  $C_0(T)$  is the equilibrium (at a fixed temperature  $T$ ) value of the concentration of the principal component in the solution, and  $k \geq 1$ . The functions  $a(T)$  and  $C_0(T)$  are given, e.g., in [6]. The parameter  $\alpha$  is usually taken within the interval  $1 \leq \alpha \leq 2$  [2, 7], though sometimes crystallization with a constant volume rate of crystal growth is considered, which corresponds to  $\alpha = 3$  [6]. The cases encountered in practice most frequently and most adequately justified theoretically are  $\alpha = 1$  (kinetic regime) [6] and  $\alpha = 2$  (diffusion regime) [8].

Equation (1.2) expresses the material balance of the principal substance in the solution. The second term on its right side corresponds to withdrawal of the principal component to crystals. According to [2], the parameter  $\rho$  is the density of crystals multiplied by  $4\pi$ . Sometimes, the concentration  $C$  is included in this multiplier [7]. For other normalizations (definitions) of the functions  $C$  and  $f$ , it is written differently. As a rule,  $\rho \gg C$ . If, in this case,  $\rho - C$  is taken instead of  $\rho$  (see [7]), the difference from the equilibrium solution is small. However, since  $d(\rho - C)/dC = -1$ , such an entry of  $C$  may significantly affect the characteristics of the neutral stability manifold. In what follows, we assume that  $\rho = \text{const}$ . The mass flux of the substance in the solution  $Q(C)$  may be taken to be constant (see [2]) in the form  $(C_* - C)/\tau$  (see [6]) ( $C_*$  is the concentration of the principal component at the entrance to the reactor) or may be written in a more complicated form if a part of the solution returns from the outlet of the system to the entrance (recrystallization) and if there are devices (classifiers) that withdraw specific fractions of crystals out of the system. The function  $Q$  is assumed to be independent of temperature.

Equation (1.3) expresses conservation of energy in the crystallization process. The parameter  $l$  is the heat released in crystallization of a unit mass of the principal substance multiplied by  $4\pi$ . In deriving Eq. (1.3), we assumed that the specific heat of the two-phase system, which is constant in the crystallization process, may be introduced.

The formulation of the problem is completed by additional conditions. In this case, it suffices to specify one boundary condition for Eq. (1.1):

$$V(C, T)r^{1-\alpha}f \Big|_{r \rightarrow 0} = J(C, T) \quad (1.6)$$

( $J$  is the intensity of nucleation). The Gibbs–Volmer formula [6] and the equation

$$J(C, T) = b(T)[C - C_0(T)]^m,$$

where the function  $b(T)$  has an “Arrhenius” form [4], are typical for the function  $J$ .

**2. Steady Solution.** Assuming that  $\partial/\partial t = 0$  in Eqs. (1.1)–(1.3) and that the other parameters, in particular, condition (1.6), are also independent of time, we obtain the relations

$$V_s \frac{d(r^{1-\alpha}f_s)}{dr} = \frac{f_* - f_s}{\tau}, \quad Q(C_s) = \rho V_s \int_0^\infty r^{3-\alpha} f_s(r) dr, \quad (2.1)$$

$$W(C_s, T_s) + lV_s \int_0^\infty r^{3-\alpha} f_s(r) dr = 0, \quad V_s r^{1-\alpha} f \Big|_{r \rightarrow 0} = J_s,$$

where the subscript  $s$  corresponds to the steady solution. The solution of the first equation of (2.1) with the boundary condition (1.6) has the form

$$F_s(\zeta) = \frac{J_s}{V_s} \exp\left(-\frac{\zeta}{\tau V_s}\right) + \frac{1}{\tau V_s} \int_0^\zeta F_*(\eta) \exp\left(\frac{\eta - \zeta}{\tau V_s}\right) d\eta, \quad (2.2)$$

where  $\zeta = r^\alpha/\alpha$  and  $F(\zeta, t) = r^{1-\alpha}f(r, t)$ , i.e., this function  $F$  may be used not only for the steady solution but also for transformation of the function  $f_*$ . From the second and third equations of (2.1), it follows that

$$\rho W(C_s, T_s) + lQ(C_s) = 0. \quad (2.3)$$

Formula (2.2) is used to obtain the moments of order  $3 - \alpha$  of the function  $f_s$  from the second equation of (2.1):

$$\frac{Q(C_s)}{\rho V_s \alpha^{\gamma-1}} = (\tau V_s)^\gamma \Gamma(\gamma) \left( \frac{J_s}{V_s} + \int_0^\infty F_*(\eta \tau V_s) \Phi(\eta) d\eta \right). \quad (2.4)$$

Equations (2.3) and (2.4) form a system of transcendental equations for the steady concentration  $C_s$  and temperature  $T_s$ . Here  $\gamma = 3/\alpha$ ,  $\Gamma(z)$  is Euler’s gamma-function [9], and the function  $\Phi(z)$  is defined by the relation

$$\Phi(z) = \Gamma(\gamma)^{-1} \exp(z) \int_z^\infty x^{\gamma-1} \exp(-x) dx = \Gamma(\gamma)^{-1} \int_0^\infty (x+z)^{\gamma-1} \exp(-x) dx.$$

We note that the function  $\Phi(z)$  may be expressed in terms of an incomplete gamma-function, which, in turn, may be represented as a particular case of the degenerate hypergeometric function [9]. For its analysis and calculation, one can use the expansions

$$\Phi(z) = \exp(z) - \sum_{n=0}^\infty \frac{z^{\gamma+n}}{\Gamma(\gamma+1+n)} = z^{\gamma-1} \sum_{n=0}^\infty \frac{z^{-n}}{\Gamma(\gamma-n)}. \quad (2.5)$$

The first expansion is a series converging everywhere, and the second one is an asymptotic (diverging for noninteger  $\gamma$ ) series. The first and second series are convenient in calculations for small and large values of  $z$ , respectively. For integer  $\gamma$ , the function  $\Phi$  is a polynomial, which can be easily derived from the second series of (2.5), since, due to the equality  $\Gamma^{-1}(-n) = 0$  ( $n = 0, 1, 2, \dots$ ) [9], the series reduces to a finite sum.

In fact, the function  $\Phi$  in (2.5) depends on the arguments  $z$  and  $\gamma$ . Since the dependence on  $\gamma$  is parametric in what follows, we do not indicate it explicitly.

In general, the solution of system (2.3), (2.4) relative to  $C_s$  and  $T_s$  can be obtained only numerically for a given function  $f_*(r)$ . For standard parameters characterized by  $Q$ ,  $W$ ,  $J$ , and  $V$ , the solution of this system exists. At the present time, it is not difficult to solve this problem. Numerous software systems were elaborated (e.g., Eureka system [10]). In the present paper, we consider the parameters  $C_s$  and  $T_s$  to be known.

**3. Basic Equation for Investigation of the Stability Characteristics of the Steady Solution.** The basic ‘‘frequency’’ equation is constructed in a similar way as was done in [11], where isothermal crystallization was analyzed in a limiting case. It is convenient to pass to the variables  $F$  and  $\zeta$  in Eqs. (1.1) and (1.2) and boundary condition (1.6). We obtain

$$\frac{\partial F}{\partial t} + V(C, T) \frac{\partial F}{\partial \zeta} = \frac{F_* - F}{\tau}, \quad (3.1)$$

$$\frac{dC}{dt} = Q(C) - \rho V(C, T) \alpha^{\gamma-1} M(F), \quad \frac{dT}{dt} = W(C, T) + lV(C, T) \alpha^{\gamma-1} M(F);$$

$$V(C, T) F \Big|_{\zeta=0} = J(C, T), \quad (3.2)$$

where  $M(F) = \int_0^\infty \zeta^{\gamma-1} F(\zeta) d\zeta$  is the moment of order  $\gamma - 1$  of the function  $F$ .

To determine the boundaries of the stability domain, we derive equations governing the evolution of a small perturbation of the steady solution. The unsteady parts of perturbations of the crystal-size distribution function, the temperature, and the oversaturation of the solution are assumed to be exponential functions of time with a complex factor  $\nu$ . This allows us to obtain the boundary of the stability domain and the frequency of arising oscillations (for the soft regime of the loss of stability, which usually occurs [2]) from the condition that the real part of the parameter  $\nu$  is equal to zero:

$$F(\zeta, t) = F_s(\zeta) + \exp(\nu t) \hat{F}(\zeta), \quad C(t) = C_s + \exp(\nu t) \hat{C}, \quad T(t) = T_s + \exp(\nu t) \hat{T}. \quad (3.3)$$

Here the hat indicates the perturbation of the steady solution. We assume that  $|\hat{F}(\zeta)| \ll F_s(\zeta)$ ,  $|\hat{C}| \ll C_s$ , and  $|\hat{T}| \ll T_s$ . Substituting expressions (3.3) into (3.1) and (3.2) and linearizing with respect to  $\hat{F}(\zeta)$ ,  $\hat{C}$ , and  $\hat{T}$ , we obtain the following equations:

$$\nu \hat{F} + V_s \frac{d\hat{F}}{d\zeta} + \left( \frac{\partial V}{\partial C} \hat{C} + \frac{\partial V}{\partial T} \hat{T} \right) \frac{dF_s}{d\zeta} + \frac{\hat{F}}{\tau} = 0; \quad (3.4)$$

$$\nu \hat{C} = \frac{dQ}{dC} \hat{C} - \rho \alpha^{\gamma-1} \left[ V_s M(\hat{F}) + \left( \frac{\partial V}{\partial C} \hat{C} + \frac{\partial V}{\partial T} \hat{T} \right) M(F_s) \right]; \quad (3.5)$$

$$\nu \hat{T} = \frac{\partial W}{\partial C} \hat{C} + \frac{\partial W}{\partial T} \hat{T} + l \alpha^{\gamma-1} \left[ V_s M(\hat{F}) + \left( \frac{\partial V}{\partial C} \hat{C} + \frac{\partial V}{\partial T} \hat{T} \right) M(F_s) \right]; \quad (3.6)$$

$$V_s \hat{F}(0) = \hat{C} \left( \frac{\partial J}{\partial C} - \frac{\partial V}{\partial C} \frac{J_s}{V_s} \right) + \hat{T} \left( \frac{\partial J}{\partial T} - \frac{\partial V}{\partial T} \frac{J_s}{V_s} \right). \quad (3.7)$$

Condition (3.7) follows from (3.2). In derivation of (3.4)–(3.7), the derivatives  $dQ/dC$ ,  $\partial W/\partial C$ ,  $\partial W/\partial T$ ,  $\partial V/\partial C$ ,  $\partial V/\partial T$ ,  $\partial J/\partial C$ , and  $\partial J/\partial T$  are calculated at the point  $(C_s, T_s)$ .

Equations (3.5) and (3.6) imply a simple relationship between temperature and concentration perturbations:

$$\rho \left( \nu - \frac{\partial W}{\partial T} \right) \hat{T} + \left[ l \left( \nu - \frac{dQ}{dC} \right) - \rho \frac{\partial W}{\partial C} \right] \hat{C} = 0. \quad (3.8)$$

Integrating Eq. (3.4) linear with respect to  $\hat{F}(\zeta)$ , substituting the result into (3.5), and taking into account relations (3.7) and (3.8) and formulas (2.2) and (2.4) for the steady case, we obtain

$$\begin{aligned} & \hat{C} \left\{ \frac{\nu - dQ/dC}{\rho\Gamma(\gamma)\alpha^{\gamma-1}} + \left( \frac{\partial J}{\partial C} - \frac{l\nu/\rho - \partial W/\partial C}{\nu - \partial W/\partial T} \frac{\partial J}{\partial T} \right) \left( \frac{V_s\tau}{1 + \nu\tau} \right)^\gamma \right. \\ & + \left( \frac{\partial V}{\partial C} - \frac{l\nu/\rho - \partial W/\partial C}{\nu - \partial W/\partial T} \frac{\partial V}{\partial T} \right) \left( \frac{V_s\tau}{1 + \nu\tau} \right)^{\gamma-1} \left[ \frac{J_s}{\nu} ((1 + \nu\tau)^\gamma - 1) \right. \\ & \left. \left. + V_s\tau \int_0^\infty F_*(V_s\tau x) \exp(x) dx \int_x^\infty \exp(-y)\Phi((1 + \nu\tau)y) dy \right] \right\} = 0. \end{aligned} \quad (3.9)$$

For noninteger values of the parameter  $\gamma$ , the functions of the form  $(1 + \nu\tau)^\gamma$  are not single-valued functions of the complex parameter  $\nu$ . Here we took a branch of the power function that is real for real values  $\nu > -1/\tau$ . For a nontrivial perturbation, we have  $\hat{C} \neq 0$ , which implies that the expression in curly braces in (3.9) is equal to zero.

Further, we restrict the stability analysis to the case without inflow of crystals from outside, i.e., we set  $F_* \equiv 0$ . Omitting  $\hat{C}$ , we write Eq. (3.9) for  $F_* \equiv 0$  as

$$Ap(p + \varkappa)(p + 1)^\gamma + p \left[ 1 - \frac{\eta(p + \xi)}{p + \sigma} \right] + \varepsilon(p + 1)[(p + 1)^\gamma - 1] \left[ 1 - \frac{\mu(p + \xi)}{p + \sigma} \right] = 0, \quad p = \nu\tau, \quad (3.10)$$

where  $A = J_s/(Q\tau\partial J/\partial C)$ ,  $\varepsilon = (\partial \ln V/\partial C)/(\partial \ln J/\partial C)$ ,  $\eta = (l\partial J/\partial T)/(\rho\partial J/\partial C)$ ,  $\mu = (l\partial V/\partial T)/(\rho\partial V/\partial C)$ ,  $\varkappa = -\tau dQ/dC$ ,  $\xi = -(\rho\tau/l)\partial W/\partial C$ , and  $\sigma = -\tau\partial W/\partial T$ . This form of the equation is convenient for analysis, because almost always the parameter  $\varepsilon \in (0, 1)$ . Since, as a rule,  $\varepsilon \ll 1$ , we may apply methods of the small parameter [12] to study the neutral stability curve and other characteristics of the process.

To construct the neutral stability manifold, one usually sets  $p = i\omega$  [2, 3, 11] in an equation of the form (3.10) and separates real and imaginary parts of the equation. Then, two equations obtained are considered. The substitution of  $p = i\omega$  into the equation that is studied to determine the stability properties of the steady solution makes it possible to obtain the frequency of oscillations in the process of the loss of stability.

In general, the procedure considered can yield not only the boundary of the stability domain but also the curves separating the domains with different numbers of roots of Eq. (3.10) with negative real parts. Therefore, among several possible branches  $\text{Re}(p) = 0$  ( $p = \nu\tau$ ), one should choose those that border upon domains where  $\text{Re}(p) < 0$  for all values of parameters, i.e., stability domains. Practical situations are simpler due to the restrictions imposed on the parameters because of physical reasons (for example, some parameters may be only positive).

It is easy to see that Eq. (3.10) always has the root  $p = 0$ , hence,  $\omega = 0$ , i.e., the loss of stability with zero frequency is possible. This case is of no interest for applications [2] and, therefore, the case  $p = 0$  ( $\omega = 0$ ) will not be considered.

**4. Solution of Eq. (3.10) for Small  $\varepsilon$ .** As was noted above, usually the parameter  $\varepsilon$  is small. This is related to a stronger dependence of the nucleation intensity (in comparison with the crystal growth rate) on oversaturation. Therefore, analysis of Eq. (3.10) for  $\varepsilon \rightarrow 0$  is of practical significance.

We substitute  $p = i\omega$  into Eq. (3.10) and seek the solution in the form of the series expansion in the small parameter  $\varepsilon$  [12]:

$$A = A_0 + \varepsilon A_1 + \varepsilon^2 A_2 + \dots, \quad \omega = \omega_0 + \varepsilon \omega_1 + \varepsilon^2 \omega_2 + \dots \quad (4.1)$$

From (3.10), after some transformations and separation of real and imaginary parts, we obtain the equations

$$A_0[(\varkappa\sigma - \omega_0^2) \cos(\gamma\varphi) - (\sigma + \varkappa)\omega_0 \sin(\gamma\varphi)] + (\sigma - \eta\xi) \cos^\gamma \varphi = 0, \quad (4.2)$$

$$A_0[(\varkappa\sigma - \omega_0^2) \sin(\gamma\varphi) + (\sigma + \varkappa)\omega_0 \cos(\gamma\varphi)] + (1 - \eta)\omega_0 \cos^\gamma \varphi = 0;$$

$$A_1 E(\varkappa, \omega_0, \gamma, \sigma) + \omega_1 H(A_0, \omega_0, \gamma, \sigma, \varkappa, \eta) = L(\omega_0, \gamma, \mu, \sigma, \xi), \quad (4.3)$$

where

$$\begin{aligned} \varphi &= \arctan \omega_0, & E &= (\varkappa + i\omega_0)(\sigma + i\omega_0)(1 + i\omega_0)^\gamma, \\ H &= iA_0[(\sigma + i\omega_0)(1 + i\omega_0)^\gamma + (\varkappa + i\omega_0)(1 + i\omega_0)^\gamma \\ &+ \gamma(\varkappa + i\omega_0)(\sigma + i\omega_0)(1 + i\omega_0)^{\gamma-1}] + i(1 - \eta), \\ L &= [1 + i\omega_0 - (1 + i\omega_0)^{\gamma+1}][1 - \mu - i(\sigma - \mu\xi)/\omega_0]. \end{aligned} \quad (4.4)$$

Separating real and imaginary parts of the complex equation (4.3) and solving the system of linear equations for  $A_1$  and  $\omega_1$ , we find that

$$A_1 = \frac{L_{\text{Re}}H_{\text{Im}} - L_{\text{Im}}H_{\text{Re}}}{E_{\text{Re}}H_{\text{Im}} - E_{\text{Im}}H_{\text{Re}}}, \quad \omega_1 = \frac{L_{\text{Im}}E_{\text{Re}} - L_{\text{Re}}E_{\text{Im}}}{E_{\text{Re}}H_{\text{Im}} - E_{\text{Im}}H_{\text{Re}}}, \quad (4.5)$$

where the subscripts Re and Im correspond to the real and imaginary parts of the functions defined by formulas (4.4). It is obvious that subsequent terms in expansions (4.1)  $A_j$ ,  $\omega_j$  ( $j \geq 2$ ) are determined by linear equations similar to (4.3) whose coefficients contain already calculated parameters. Here we restrict the analysis to the leading approximation (4.2), which determines the behavior of the stability characteristics of the system and enables us to obtain corrections  $A_1$  and  $\omega_1$  from Eqs. (4.4) and (4.5).

In turn, in several limiting cases, formulas (4.2)–(4.5) can be simplified. The influence of thermal effects on the stability of the crystallized polydisperse system can be easily traced if some parameters characterizing these effects are small.

Let us consider the case  $|\eta| \ll 1$ . We assume that  $\sigma = O(1)$ ,  $\xi = O(1)$ , and  $\varkappa = 0$ , i.e., the inflow of mass  $Q$  in the solution is independent of oversaturation (see, e.g., [2, 7]). Expanding relations (4.2) into power series in  $\eta$  and restricting ourselves to the first two terms, after some transformations we obtain

$$\varphi = \frac{\pi}{2\gamma} - \frac{\eta\{\sigma - \xi \tan[\pi/(2\gamma)]\}}{\gamma\{\sigma^2 + \tan^2[\pi/(2\gamma)]\}}, \quad (4.6)$$

$$A_0 = \frac{\cos^\gamma[\pi/(2\gamma)]}{\tan[\pi/(2\gamma)]} \left\{ 1 - \eta \left[ 1 - \frac{(\sigma - \xi) \tan[\pi/(2\gamma)]}{\sigma^2 + \tan^2[\pi/(2\gamma)]} \left( \frac{\sigma}{\tan[\pi/(2\gamma)]} + \tan \frac{\pi}{2\gamma} + \frac{2}{\gamma \sin^2(\pi/\gamma)} \right) \right] \right\}.$$

These expressions are valid if the parameter  $\gamma$  differs from unity. As was noted above, the case  $\gamma = 1$  is encountered in practice [6]. In this case, it is better to use Eq. (3.10), which for  $\gamma = 1$  becomes a fourth-degree polynomial with one known root  $p = 0$ , i.e., in fact, a polynomial of the third degree. For polynomials, there are simple criteria (for example, the Hurwitz criterion [13]) for determining the location of roots in the left half-plane of the complex variable  $p$ , which are reduced to a set of inequalities. These inequalities can be checked easily; therefore, the case  $\gamma = 1$  is not considered here. In a certain sense, this is the simplest version of the equations of crystallization. If the parameter  $\gamma$  is close to unity, it is not difficult to obtain corrections to the case  $\gamma = 1$  using the perturbation method. We note that Eq. (3.10) reduces to a polynomial not only for  $\gamma = 1$  but also for  $\gamma = 2$  and 3 ( $\gamma = 3$  corresponds to the kinetic regime) from the range of  $\gamma$  of interest to us. Both these regimes occur in practice.

Both relations (4.2)–(4.5) and their limit case (4.6) describe only one branch of the neutral stability curve  $\text{Re}(p) = 0$ , which is connected with the order of terms in expansion (4.1). This follows, for instance, from relations (4.2), which become indefinite as  $A_0 \rightarrow 0$ ,  $\varphi \rightarrow \pi/2$ , and  $\omega_0 \rightarrow \infty$ . Thus, the solution in the form (4.1) does not represent all solutions of Eq. (3.10). To construct another branch of the neutral stability curve  $\text{Re}(p) = 0$ , we substitute  $p = i\omega$  into (3.10), separate real and imaginary parts, and exclude the parameter  $A$  from the system of equations obtained. After some transformations, we obtain the expression ( $\psi = \arctan \omega$ )

$$\begin{aligned}
& \sin \psi \cos^\gamma \psi \left\{ \omega(1 - \eta)[(\varkappa\sigma - \omega^2) \cos(\gamma\psi) - (\sigma + \varkappa)\omega \sin(\gamma\psi)] - (\sigma - \eta\xi)[(\varkappa\sigma - \omega^2) \sin(\gamma\psi) \right. \\
& \left. + (\sigma + \varkappa)\omega \cos(\gamma\psi) \right\} + \varepsilon \left\{ (1 - \mu)(\varkappa\sigma - \omega^2 - \sigma - \varkappa)\omega \sin \psi - (\sigma - \mu\xi) \left[ (\varkappa\sigma - \omega^2) \{ \cos[(2\gamma + 1)\psi] \right. \right. \\
& \left. \left. - \cos[(\gamma + 1)\psi] \cos^\gamma \psi \} - (\sigma + \varkappa)\omega \{ \sin[(2\gamma + 1)\psi] - \sin[(\gamma + 1)\psi] \cos^\gamma \psi \} \right] \right. \\
& \left. + (1 - \mu)\omega \cos^\gamma \psi \left[ (\varkappa\sigma - \omega^2) \sin[(\gamma - 1)\psi] + (\sigma + \varkappa)\omega \cos[(\gamma - 1)\psi] \right] \right\} = 0. \quad (4.7)
\end{aligned}$$

If we set  $\varepsilon = 0$  in (4.7), the equality of the expression in the first curly braces to zero follows from formulas (4.2), i.e., expansion (4.1) is related to this branch of the solution of Eq. (3.10). The second branch is defined by the equality  $\cos^\gamma \psi = 0$ , i.e.,  $\psi = \pi/2$  in the main approximation. The case  $\sin \psi = 0$ , i.e.,  $\omega = 0$ , is not considered here. Writing a new expansion in the form

$$A = \varepsilon^{1+1/\gamma}(\tilde{A}_0 + \varepsilon\tilde{A}_1 + \dots), \quad \omega = \varepsilon^{-1/\gamma}(\tilde{\omega}_0 + \varepsilon\tilde{\omega}_1 + \dots) \quad (4.8)$$

and assuming that  $1 < \gamma < 3$ , we obtain

$$\tilde{\omega}_0 = [(1 - \eta) \cos(\pi\gamma/2)/(\mu - 1)]^{1/\gamma}, \quad \tilde{A}_0 = (\mu - 1) \tan(\pi\gamma/2), \quad (4.9)$$

$$\tilde{\omega}_1 = \tan(\pi\gamma/2)[\tilde{\omega}_0(\varkappa + \sigma + \gamma) - (\sigma - \eta\xi)/(1 - \eta)]/\gamma;$$

$$\tilde{A}_1 = \tilde{\omega}_0^{-2-\gamma} \left[ (\sigma - \eta\xi) \cos \frac{\pi\gamma}{2} + (1 - \eta)\gamma\tilde{\omega}_1 \sin \frac{\pi\gamma}{2} \right] + \frac{(1 - \mu)[1 + \gamma + (\sigma - \mu\xi)/(1 - \mu)]}{\tilde{\omega}_0^2} - \frac{\tilde{A}_1\tilde{\omega}_1}{\tilde{\omega}_0}. \quad (4.10)$$

Formulas (4.9) and (4.10) are derived from (3.10) for  $p = i\omega$  by separating real and imaginary parts, expanding into a power series in the parameter  $\varepsilon$ , and regrouping terms of the same order in  $\varepsilon$ .

Formulas (4.8)–(4.10) are simple in structure and need no further simplifications. Simplifications of Eqs. (4.2) related to the smallness of other (not  $\eta$ ) parameters that characterize thermal effects in the mass crystallization process are not considered here.

**5. Examples of Calculations.** Figures 1 and 2 show the solutions of Eqs. (4.2) for  $\eta = O(1)$ . System (4.2) itself is not complicated for analysis, and the problem of its interpretation lies only in the presence of a large number of parameters. Figures 1–4 show the calculation results for  $\xi = 0$ ,  $\varepsilon = 0$ ,  $\varkappa = 0$ , and  $\gamma = 2$  ( $\alpha = 3/2$ ). The case of  $\alpha = 3/2$  is of practical interest because it is observed in crystallizers for Reynolds numbers greater than 500 [14]. In this case, for the frequency of arising oscillations  $\omega$  and the parameter  $A$  characterizing the influence of incipient particles on the stability of the steady solution, one can obtain the following analytical expressions from formulas (4.2):

$$A = \frac{\sigma^3 + 2\sigma^2 + \sigma - 2 + (\sigma + 2)P + \eta(2\sigma^2 + 3\sigma + 2)}{4\sigma(\sigma + 1)^2}, \quad (5.1)$$

$$\omega = \sigma / \{ [\sigma^2 - 1 + P + \eta(2\sigma + 1)] / 2 \}^{1/2}.$$

Here  $P = \{ [\sigma^2 + 1 + \eta(2\sigma + 1)]^2 - 4\eta(\sigma + 1)^2 \}^{1/2}$ . In (5.1), the arithmetic value of the root is used. It can be shown that, if we choose the minus sign before  $P$ , the expression for the parameter  $A$  is negative. This event ( $A < 0$ ), known as Tamman's effect [2, 15], rarely occurs in practice. In this case,  $\partial J / \partial C < 0$ , which leads to the inequality  $A < 0$ . This case is not considered here. Apart from  $\partial J / \partial C > 0$ , the inequality  $\partial J / \partial T > 0$  is also valid; therefore,  $\eta = (l\partial J / \partial T) / (\rho\partial J / \partial C) > 0$ . In what follows, we consider only the case  $\eta > 0$ . The intensity of the heat influx into the crystallizing system is usually defined by the expression [3]  $W(T) = K(T_t - T)$ , which is used in analysis of bubble boiling ( $T_t$  is the thermostat temperature and  $K$  is the effective heat-exchange coefficient). For the crystallization process, this function may be supplemented by the term  $(T_* - T) / \tau$ , where  $T_*$  is the temperature at the entrance to the system, which, in general, may not coincide with  $T_t$ . The situation where  $\sigma = -\tau\partial W / \partial T > 0$  is typical; therefore,  $\sigma$  is considered below to be a positive parameter. The equality of the parameter  $\varkappa$  to zero means that  $Q = \text{const}$ . This case is considered in [2].

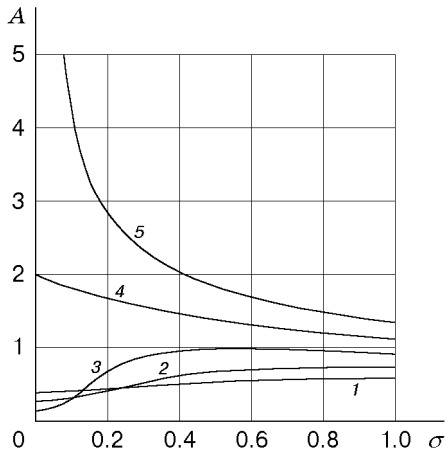


Fig. 1

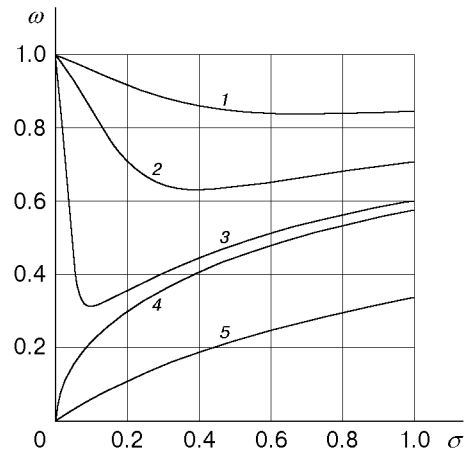


Fig. 2

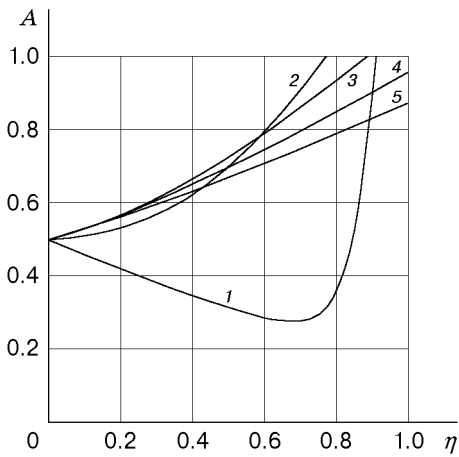


Fig. 3

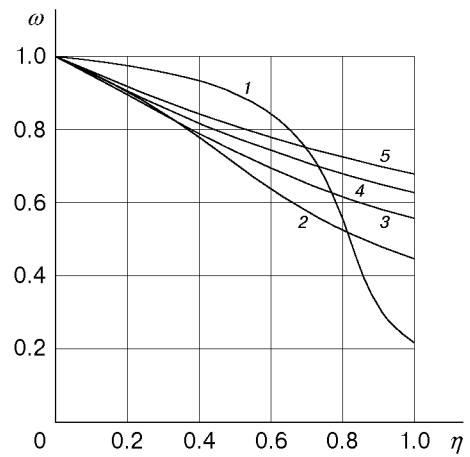


Fig. 4

Expressions (5.1) are complicated for analysis. Some limiting cases are of interest. Figure 1 shows the function  $A(\sigma)$  for  $\eta = 0.25, 0.5, 0.75, 1.0$ , and  $1.25$  (curves 1–5, respectively). The stability domain lies above the curves along the  $A$  axis. Curve 4 is delimiting in character, it separates curves with a finite limit for  $\sigma \rightarrow 0$  ( $\eta < 1$ ) from curves that have the  $A$  axis as a vertical asymptote. The equation of curve 4 ( $\eta = 1$ ) has the form  $A(\sigma, 1) = [(\sigma + 2)/(\sigma + 1)]^2/2$ . As  $\sigma \rightarrow 0$  (curves 1–3), the function  $A$  has the following asymptotic behavior:  $A(\sigma, \eta) = (1 - \eta)/2 + O(\sigma)$ . As  $\sigma \rightarrow 0$  ( $\eta > 1$ ), the function  $A$  has the form  $A(\sigma, \eta) = (\eta - 1)/\sigma + 2 + O(\sigma)$ . For large  $\sigma$  ( $\sigma \rightarrow \infty$ ), we have  $A(\sigma, \eta) = 1/2 + 2/\sigma + 15/(4\sigma^2) + \eta(1/\sigma + 3/\sigma^2) + O(\sigma^{-3})$ . This result is independent of whether the parameter  $\eta$  is smaller or larger than unity.

Figure 2 shows the frequency of self-induced oscillations appearing when the system loses stability versus the parameter  $\sigma$  for  $\eta = 0.3, 0.6, 0.9, 1.0$ , and  $3.0$  (curves 1–5, respectively). As in Fig. 1, curve 4 separates families of curves. For  $\eta < 1$ , the curves leave the point  $(\sigma = 0, \omega = 1)$ , and for  $\eta > 1$ , curves leave the origin. The equation of curve 4 has the form  $\omega(\sigma, 1) = [\sigma/(\sigma + 2)]^{1/2}$ . The asymptotic form of the function  $\omega(\sigma, \eta)$  for  $\sigma \rightarrow 0$  can be written as follows:  $\omega(\sigma, \eta) = 1 - \sigma\eta/(1 - \eta) + O(\sigma^2)$  for  $\eta < 1$  and  $\omega(\sigma, \eta) = \sigma(\eta - 1)^{-1/2}[1 + \sigma\eta/(1 - \eta) + O(\sigma^2)]$  for  $\eta > 1$ . For large values of the parameter  $\sigma$ , independently of whether the parameter  $\eta$  is smaller or larger than unity, the following asymptotic formula is valid:  $\omega(\sigma, \eta) = 1 - \eta/\sigma + O(\sigma^{-2})$  as  $\sigma \rightarrow \infty$ . On curves 1–3 (Fig. 2), the minimum value  $\omega_{\min} = \sigma^{1/2}$  is attained at the points  $\sigma = 1 - \eta$ .

Figure 3 shows the function  $A(\eta)$  for  $\sigma = 0.1, 0.6, 1.1, 1.6$ , and  $2.1$  (curves 1–5, respectively). As  $\eta \rightarrow 0$ , we have  $A(\sigma, \eta) = 1/2 + \eta(\sigma - 1/2)/(1 + \sigma^2) + O(\eta^2)$ . For large values of the parameter  $\eta$ , we obtain  $A(\sigma, \eta) = [\sigma^2 - 1 + \eta(2\sigma + 1)]/[\sigma(2\sigma + 1)] + O(\eta^{-1})$ , i.e., the graph of the asymptote is a straight line. As in Fig. 1, the stability domain lies above the curves along the  $A$  axis.



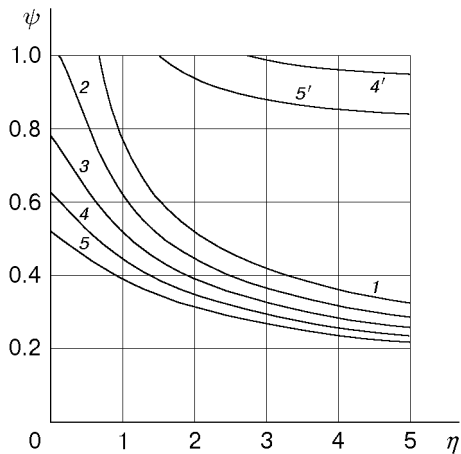


Fig. 5

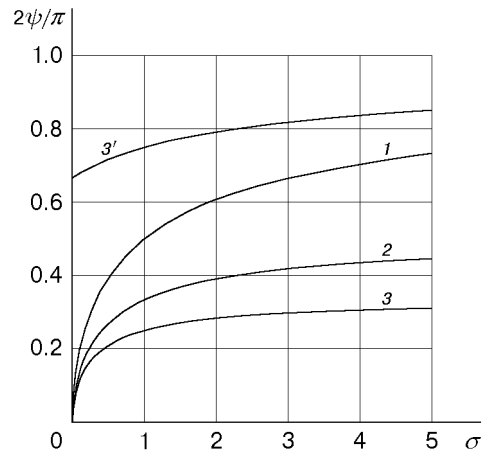


Fig. 6

Figure 4 shows the frequency of self-induced oscillations that appear when the system loses stability versus the parameter  $\eta$  for  $\sigma = 0.1, 0.5, 0.9, 1.3,$  and  $1.7$  (curves 1–5, respectively). In the region of small values of the parameter  $\eta$ , we have  $\omega(\sigma, \eta) = 1 - \sigma\eta/(1 + \sigma^2) + O(\eta^2)$  as  $\eta \rightarrow 0$ . For large values of  $\eta$  and fixed  $\sigma$ , the asymptotic form of the function  $\omega(\sigma, \eta)$  is written as  $\omega(\sigma, \eta) = \sigma[\eta(2\sigma + 1)]^{-1/2}\{1 - (2\sigma^3 - 2\sigma - 1)/[\eta(2\sigma + 1)]^2 + O(\eta^{-2})\}$  ( $\eta \rightarrow \infty$ ).

Figure 5 shows the angle  $\psi$  ( $\psi = \arctan \omega$ ) as a function of the parameter  $\eta$  for  $\varepsilon = 0, \xi = 0, \varkappa = 0, \sigma = 1,$  and  $\gamma = 1.0, 1.5, 2.0, 2.5,$  and  $3.0$  (curves 1–5, respectively). The calculation was performed using formula (4.7), which, for the specified values of the parameters  $\varepsilon, \xi, \varkappa,$  and  $\sigma$ , has the form  $\omega(1 - \eta)[\omega \cos(\gamma\psi) + \sigma \sin(\gamma\psi)] = \sigma[\sigma \cos(\gamma\psi) - \omega \sin(\gamma\psi)]$ . Figure 5 implies that the function  $\psi(\eta)$  is not single-valued. We should note that curves 4' and 5' correspond to  $A < 0$ , which is rarely observed in practice.

Figure 6 shows the function  $\psi(\sigma)$  for  $\varepsilon = 0, \xi = 0, \varkappa = 0, \eta = 1,$  and  $\gamma = 1.0, 2.0,$  and  $3.0$  (curves 1–3, respectively). Curve 3' corresponds to  $A < 0$ . The calculation was performed using the same formula as for the curves in Fig. 5. For the specified values of the parameter  $\gamma$ , analytical expressions for the functions  $\psi(\sigma)$  can be obtained.

In general, the stability analysis of the steady solution for  $F_* \neq 0$  in Eq. (3.9) comes across a number of difficulties. We mention the simplest case (that is of practical importance) of  $F_* = N\delta(\zeta + 0)$ , where  $N$  is the number of crystals and  $\delta(\zeta)$  is the Dirac delta-function. It can be shown using the properties of the Dirac delta-function that, in terms of the variables  $f$  and  $r$ , the function  $f_*$  has a similar form  $f_* = N\delta(r + 0)$ . The physical meaning of this expression corresponds to the case where a monodisperse fraction of negligible size arrives at the entrance of a crystallizer (for example, a fraction of crystals continuously supplied from another crystallizer). Calculation of the integral in formula (3.9) yields the quantity  $N[(1 + \nu\tau)^\gamma - 1]/(\nu\tau)$ , which, as one can easily see, corresponds to the increase in the nucleation intensity  $J_s$  in this formula by the quantity  $N/\tau$ . Thus, supplying a monodisperse fraction of negligible size to the entrance of a crystallizing system is equivalent to imaginary nucleation with intensity  $N/\tau$ , which clarifies the physical meaning of the function  $f_* = N\delta(r + 0)$ . This means that Eq. (3.10) retains its form. Only the value of the parameter  $A$  changes. Therefore, there is no need for a separate investigation of stability of the steady solution with a given input function  $f_*$ .

**6. Conclusions.** Thus, a transcendental equation for the frequency of arising self-induced oscillations was obtained for investigation of stability of the steady solution of the problem of nonisothermal mass crystallization in the general case. For several examples, the results of the solution of this equation obtained by asymptotic methods are presented.

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