

A LIMITING REGIME OF CRYSTALLIZATION OF A POLYDISPERSE SYSTEM FROM SOLUTIONS

A. I. Moshinskii

UDC 548.01:66.065

The description of a polydisperse system of particles with a phase transition is of interest for the study of a number of natural and technological particles. Examples in point are the growth of fog droplets during condensation, the reverse process of disappearance of drops because of evaporation, crystallization, and dissolution of solid particles in a solution given some supersaturation (undersaturation), etc. The mathematical models of such processes contain common elements and as a result similar logarithms are used to study them.

The most complete description of this range of phenomena is given by methods of the mechanics of heterogeneous media [1-3]. The application of this method, however, entails some difficulties and also requires the use of some closing relations, which often has an uncontrolled effect on the accuracy of the calculations. In practice, therefore, another approach is used extensively, involving the introduction of the size distribution function of the particles. Knowledge of the distribution function makes it possible to find the time variation of all of the quantities of interest for the application: the number of particles, their average size, specific surface, the total volume of all the particles of the solid phase, etc. An idea of the approaches to the given nonlinear problems can be obtained from [4-9]. A distinctive feature of the processes analyzed in the references cited is the absence of external particle source and sinks; as a result the system evolves until supersaturation or some other (analogous) driving force of the process disappears altogether. When substance is introduced into and/or taken out of the continuous and disperse phases the problem becomes more complicated and takes on new qualitative features. Under certain conditions, for example, a steady state loses stability and oscillatory phenomena develop [10-14]. In such problems the stability of the process and the dynamics of the transient phenomena upon a sudden change in parameters become paramount.

In this study we consider the limiting solution of the problem of crystallization when a solution containing the crystallizing solution is fed in and part of the crystals is carried out of the system with the flow.

1. Formulation of the Problem. With vigorous mixing the particle size distribution function F depends only on the crystal size r and the time τ . The main balance equation for the number of crystals is written as

$$\partial F / \partial \tau + UG \partial (F/r^\alpha) / \partial r = -F(r, \tau) / \tau_1, \quad (1.1)$$

where the crystal growth rate is taken to be

$$dr/d\tau = UG/r^\alpha, \quad U = \text{const}, \quad \alpha = \text{const}. \quad (1.2)$$

The growth rate is assumed to be proportional to the supersaturation G of the solution, although more complex laws used in practice, in particular power laws, would not pose any fundamental problem.

Supersaturation is constructed here to mean the difference between the instantaneous and equilibrium concentrations of the substance precipitated in the solution, i.e., the absence of supersaturation corresponds to $G = 0$. The value of the constant α depends on the conditions of the mass transfer of crystals with the carrier medium. Most often the theoretically substantiated laws of kinetic crystal growth ($\alpha = 0$ [8, 11, 12]) and "diffusion" growth ($\alpha = 1$ [13, 15, 16]).

The dissolution of particles can also be described by using Eq. (1.2) for a negative U . A change in the sign of U rearranges the field of characteristics of Eq. (1.1) and an auxiliary condition for r becomes necessary. On the whole, this facilitates the analysis. Next we assume that $U > 0$. The influx of particles into the system (besides the nucleation mechanism) will not be considered here. The parameter τ_1 express the characteristic time of crystal transport through the apparatus. It is equal to the ratio of the crystallizer volume to the volume flow rate of the solid phase.

The second equation, which must be solved along with (1.1), expresses the balance of the largest substance in the solution and has the form

$$dG/d\tau = -\beta UG \int_0^{\infty} r^{2-\alpha} F(r, \tau) dr + \kappa (G_* - G)/\tau_1. \quad (1.3)$$

The constant β in (1.3) characterizes the shape of the crystals, their density, etc. A definition of it is given, e.g., in [14]. The rate at which the substance passes from the solution into the solid phase is determined by the second term of Eq. (1.3). The substance may be transported, generally speaking, at a different rate. This takes into account the parameter κ , which is equal to the ratio of the flow rate of the target substance in the solution to that of substance in the crystals. The quantity G_* is assumed to be constant.

Equations (1.1) and (1.3) supplement the initial and boundary conditions

$$F|_{\tau=0} = F^0(r), \quad G|_{\tau=0} = G^0, \quad F/r^\alpha|_{r=0} = JG^m/(UG), \quad (1.4)$$

where JG^m is the nucleation rate (J and m are constants). Here we take the power law customarily used in practice for the nucleation rate of the new phase. We introduce the dimensionless variables and parameters

$$f = F\beta\rho^4/G^0, \quad f^0 = F^0\beta\rho^4/G^0, \quad C = G/G_0, \quad C_* = G_*/G^0, \quad (1.5)$$

$$\tau_2 = \rho^{\alpha+1}/UG^0, \quad t = \tau/\tau_2, \quad \varepsilon = \tau_2/\tau_1, \quad z = r/\rho$$

(ρ is the scale for the crystal size, which can be determined, e.g., from the nature of the variation of the initial distribution function $F^0(r)$). In the variables (1.5) the problem (1.1)-(1.4) is written as

$$\partial f/\partial t + C\partial(f/z^\alpha)/\partial z = -\varepsilon f(z, t); \quad (1.6)$$

$$dC/dt = -C \int_0^{\infty} z^{2-\alpha} f(z, t) dz + \varepsilon\kappa(C_* - C); \quad (1.7)$$

$$f|_{t=0} = f^0(z), \quad C|_{t=0} = 1, \quad f/z^\alpha|_{z=0} = BC^n \quad (1.8)$$

$$(B = J\beta\rho^{\alpha+4} (G^0)^{m-2}/U, \quad n = m - 1).$$

Equations (1.5) shows that the problem (1.1)-(1.4) contains two characteristic times τ_1 and τ_2 . Some terms or others will predominate in particular time intervals, depending on the ratios of these scales. Below we consider the variant $\varepsilon \ll 1$ and construct the solution of the problem (1.6)-(1.8) by the method of small perturbations [17].

2. The Solution for the Time Scale τ_2 . Looking for the solution of the problem in the form of a series

$$f = f_0(z, t) + \varepsilon f_1(z, t) + \dots, \quad C = C_0(t) + \varepsilon C_1(t) + \dots, \quad (2.1)$$

and then substituting them into Eqs. (1.6)-(1.8) and separating the terms of the same order in ε , in the main approximation in ε we arrive at the problem

$$\partial f_0/\partial t + C_0\partial(f_0/z^\alpha)/\partial z = 0; \quad (2.2)$$

$$dC_0/dt = -C_0 \int_0^{\infty} z^{2-\alpha} f_0(z, t) dz; \quad (2.3)$$

$$f_0|_{t=0} = f^0(z), \quad C_0|_{t=0} = 1, \quad f_0/z^\alpha|_{z=0} = BC_0^n. \quad (2.4)$$

We introduce the moment characteristics of the function f_0 (and of other functions in similar fashion) using the formula

$$\langle f_0 \rangle_j = \int_0^{\infty} z^j f_0(z, t) dz. \quad (2.5)$$

It is readily seen that the system (2.2), (2.3) has the integral

$$3C_0 + \langle f_0 \rangle_3 = 3 + \langle f^0 \rangle_3 = \text{const.} \quad (2.6)$$

The main approximation in ε for the problem (1.6)-(1.8) (the system (2.2), (2.4), (2.6)) is a characteristic problem of periodic mass crystallization, which for various values of the parameters) has been considered in the literature a number of times (see e.g., [8, 9, 18]). Both exact and approximate solutions of the problem (2.2), (2.4), and (2.6) were obtained in the references cited and other studies. Accordingly, we assume that the solution of the given problem (e.g., the function f_0 , etc.) is known.

Let us note a fact established earlier [9]. The solution of the problem, i.e., the function $f_0(z, t)$ tends to the equilibrium value $f_0(z, \infty)$ as $t \rightarrow \infty$. Here C_0 tends to zero. The function C does not reach zero but tends to a constant value of the first order in the small parameter ε . The distribution function f has f_0 as an "intermediate" limit. After the solution reaches $f_0(z, \infty)$ the function f begins to evolve more slowly with a characteristic time τ_1 or, in the terminology of [17], changes in the system take place with an "external time" $T = \tau/\tau_1 = \varepsilon t$. It thus becomes necessary to construct an "external" expansion for a more complete description of the problem.

3. The Stationary Solution. First we consider the stationary solution of the problem (1.1), (1.3), (1.4). This gives an idea of the orders of magnitude of the main variables, which form at fairly large values of time. We introduce the new variables

$$\psi(\zeta, t) = f(z, t)/z^\alpha, \quad \zeta = z^{\alpha+1}/(\alpha+1). \quad (3.1)$$

It can be easily shown that the moments of the function f in the variable z and the moments of function ψ in ζ are related by [9]

$$\langle f \rangle_j = (\alpha+1)^{j/(\alpha+1)} \langle \psi \rangle_{j/(\alpha+1)}. \quad (3.2)$$

The stationary equation (1.6) has the integral

$$\psi_\infty(\zeta) = BC_\infty^n \exp(-\varepsilon\zeta/C_\infty), \quad (3.3)$$

written in the variables (3.1), where, in order to determine the unknown value of the supersaturation at equilibrium C_∞ by means of the stationary equation (1.7), we obtain the relation

$$C_\infty (1+\alpha)^\gamma \langle \psi \rangle_\gamma = B\Gamma(1+\gamma) (1+\alpha)^\gamma C_\infty^{n+\gamma+2} = \varepsilon\kappa (C_* - C_\infty) \quad (3.4)$$

($\gamma = (2-\alpha)/(1+\alpha)$, $\Gamma(z)$ is the Euler gamma function). From (3.4) we easily see that, first, when all the parameters have positive values of practical interest this equation is uniquely solvable in C_∞ . Second, for small values of ε the quantity C_∞ is also small and from (3.4) we get the approximation

$$C_\infty \approx \{\varepsilon\kappa C_* / [B\Gamma(1+\gamma) (1+\alpha)^\gamma]\}^{1/(n+2+\gamma)}. \quad (3.5)$$

This expression shows the order of C_∞ in ε and when substituted into (3.3) also gives the order for the function $\psi_\infty(\zeta)$.

4. The Solution for Time Scale τ_1 . As mentioned above, when the system (2.2)-(2.4) is solved the function C_0 of the main approximation tends to zero as $t \rightarrow \infty$ while f_0 remains a finite quantity. From the equation for C_1

$$dC_1/dt = -C_0 \langle f_1 \rangle_{2-\alpha} - C_1 \langle f_0 \rangle_{2-\alpha} + \kappa (C_* - C_0)$$

we can expect C_1 to be finite as $t \rightarrow \infty$, i.e., we can expect that $C_1 \rightarrow \kappa C_* / \langle f_0(z, \infty) \rangle_{2-\alpha}$ (we will not study an approximation of the order of ε), on the assumption that $dC_1/dt \rightarrow 0$ as $t \rightarrow \infty$; the natural order with the time scale τ_1 , therefore, will be ε for the expansion of the saturation and $O(1)$ in ε for the distribution function, as follows from the joining principle [17].

One more important remark. Equation (2.2) and Eq. (4.4) obtained below are hyperbolic and by virtue of this in crystallization problems the effect of the initial and boundary conditions in the variables t and z , etc. extends in known degree,

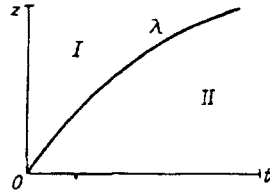


Fig. 1

each in its own region. These regions are separated by a characteristic that emerges from the origin $dz/dt = C, z|_{t=0} = 0$ (Fig. 1). Similar problems are also considered, e.g., in [19]. This characteristic is labeled by λ in Fig. 1, and this label will be used below. In actual fact, an "interaction" of the solutions with each other in each of these regions does occur through the intermediary of the function C , which is the same for the entire volume of the binary system. It is important that the scales of f at each of the two regions are determined by their auxiliary condition. While this was not noticeable for the solution of Sec. 2, since the orders of the initial and boundary conditions were assumed to be of the same order, on passage to the time scale τ_1 , when $C = O(\epsilon)$, the boundary condition (1.8) dictates that the distribution have the order $f = O(\epsilon^n)$. This pertains only to region II in Fig. 1, while the discussion of the preceding paragraph pertains to region I, i.e., joining by the time variable is effected for it. We thus find that for times of the order of τ_1 the main approximation must be constructed in the form

$$C(T) = \epsilon C^*(T) + \dots, \quad f^* = \begin{cases} f_I^*(z, T) + \dots & \text{for zone I,} \\ \epsilon^n f_{II}^*(z, T) + \dots & \text{for zone II,} \end{cases} \quad (4.1)$$

where the asterisk denotes expansion on the scale of τ_1 . Substituting (4.1) into (1.6)-(1.8), written for $T = \epsilon t$ in the form

$$\partial f / \partial T + (C/\epsilon) \partial (f/z^\alpha) / \partial z = -f(z, T); \quad (4.2)$$

$$dC/dT = - (C/\epsilon) \int_0^\infty z^{2-\alpha} f(z, T) dz + \kappa (C_* - C), \quad (4.3)$$

we arrive in the main approximation to the problem

$$\partial f^* / \partial T + C^* \partial (f^*/z^\alpha) / \partial z = -f^*(z, T); \quad (4.4)$$

$$C^*(T) \int_0^\infty z^{2-\alpha} f^*(z, T) dz = \kappa C_* = C^*(T) \langle f^* \rangle_{2-\alpha}; \quad (4.5)$$

$$f_I^*|_{T=0} = f_0(z, \infty), \quad f_{II}^*/z^\alpha|_{z=0} = B(C^*)^n. \quad (4.6)$$

Equation (4.3) in the main approximation assumed the "stationary" form (4.5) and so an initial condition is not necessary for C^* . The initial condition for (4.4) was obtained by the limiting joining procedure [17]. Equation (4.4) is written in the same way for regions I and II, which is why the lower indices are omitted there. The moment $\langle f^* \rangle_{2-\alpha}$ consists of two parts:

$$\langle f^* \rangle_{2-\alpha} = \int_\lambda^\infty z^{2-\alpha} f_I(z, T) dz + \int_0^\lambda z^{2-\alpha} f_{II}(z, T) dz. \quad (4.7)$$

Here the function $\lambda(T)$ is the same characteristic separating the two regions (see Fig. 1), which is given by the equation

$$d\lambda/dT = C^*, \quad \lambda|_{T=0} = 0. \quad (4.8)$$

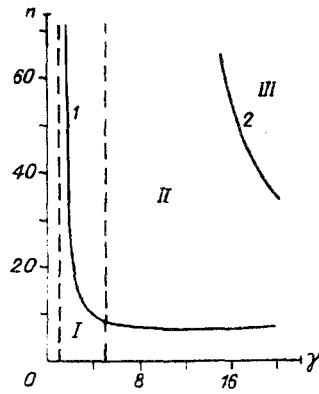


Fig. 2

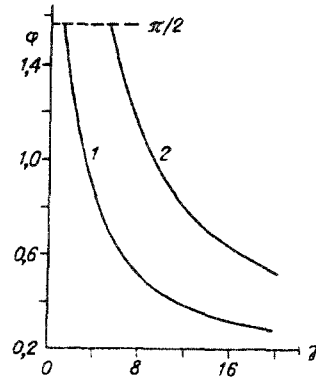


Fig. 3

Next we assume that $C_* \neq 0$; otherwise, the problem simplifies appreciably since from (4.5) we find that $C^* = 0$ and (4.4) in essence becomes an ordinary differential equation.

The problem (4.4)-(4.6) is not final in the sense that its solution does not reach a stationary regime (3.3). The point is that with time the significance of the terms in (4.7) changes. While in the initial stage the second term (of the order of ε^n) can be ignored the mechanism of extracting particles from the system (the last term in (4.4)) leads to an appreciable decrease in f^*_I . Like the growth of the lower limit of $\lambda(T)$ in the first integral term (4.7), this leads to a decrease in the second term. The second term in (4.7) is gradually "topped up" by nucleation, which is expressed by the boundary condition (4.6). When the time are rather long the role of this term becomes dominant and with time the solution in region II of Fig. 1 goes over into the solution for the stationary regime. Equations (3.3) and (3.5) show what orders of the main variables should have upon entry into the stationary solution. These orders do not coincide with those chosen in (4.1), i.e., (4.4)-(4.6) describe the intermediate stage in the development of the process.

If we disregard the solution in region II as being small in comparison with the solution in region I and go over to variables of the type (3.1) for f^* and z , the problem (4.4)-(4.6) is written as

$$\partial \psi^* / \partial T + (d\lambda / dT) \partial \psi^* / \partial \zeta = -\psi^*; \quad (4.9)$$

$$\langle \psi^* \rangle_\gamma = \omega dT / d\lambda, \quad \omega = \kappa C_* / (1 + \alpha)^\gamma; \quad (4.10)$$

$$\psi^* |_{T=0} = \psi_0(\zeta, \infty) = f_0(z, \infty) / z^\alpha, \quad \psi^* |_{\zeta=0} = 0, \quad (4.11)$$

where Eqs. (3.2) and (4.8) were used. The distribution function is expressed after solving Eq. (4.9) (in which temporarily $\lambda(T)$ is assumed to be known) by

$$\psi^*(\zeta, T) = \exp(-T) \psi_0[\zeta - \lambda(T)] H[\zeta - \lambda(T)] \quad (4.12)$$

($H(z) = \begin{cases} 1, & z > 0, \\ 0, & z < 0 \end{cases}$ is the Heaviside function). The moment of the order of γ in the function ψ^* (4.12) is calculated and

substitution of the result into (4.10) leads to an equation for determining $\lambda(T)$:

$$\omega dT / d\lambda = \exp(-T) \int_0^\infty [\zeta + \lambda(T)]^\gamma \psi_0(\zeta, \infty) d\zeta, \quad T|_{\lambda=0} = 0; \quad (4.13)$$

it has the solution

$$T = \ln \left\{ 1 + \frac{1}{\omega(1+\gamma)} \int_0^\infty \psi_0(\xi, \infty) [(\xi + \lambda)^{\gamma+1} - \xi^{\gamma+1}] d\xi \right\}, \quad (4.14)$$

as can be ascertained by a direct check. Equations (4.12) and (4.14) solve the problem (4.9)-(4.11) in parametric form in terms of the parameter λ . The expression for the moments of any order j is also fairly simple:

$$\langle \psi^* \rangle_j = \int_0^\infty \psi_0(\xi, \infty) (\xi + \lambda)^j d\xi \left\{ 1 + \frac{1}{\omega(1+\gamma)} \int_0^\infty \psi_0(\xi, \infty) \times \right. \\ \left. \times [(\xi + \lambda)^{\gamma+1} - \xi^{\gamma+1}] d\xi \right\}^{-1}. \quad (4.15)$$

Without specifying the class of functions $\psi_0(\xi, \infty)$, we can ascertain from the simplest samples that $\lambda(T)$ tends monotonically (the monotonicity is clear from (4.13)) to infinity with time, which accords with what was said above. With (4.14) it is also rather simple to track the evolution of the moments (4.15) with time.

A distinctive feature of the problem under consideration is that the order the sought quantities in ε change substantially for the same time scale τ_1 . Since the objective is to obtain the main approximation to the solution of the problem, there is no need to construct additional expansions, etc.; it is sufficient in the respective equations not to make the passage to the limit $\varepsilon \rightarrow 0$ in cases when the terms simplified in this manner still manifest themselves substantially in a range of the parameters. In this problem at times of the order of τ_1 this concept leads to the system of equations (4.9)-(4.11) when $B(\varepsilon C^*)^n$ is substituted for the right side of the boundary condition. This system can be written as a single equation for the function ψ , where the superscript asterisk of ψ as well as of C is henceforth omitted for simplicity. The problem of the evolution of a crystallizing system for times of the order of τ_1 thus is written as

$$\partial \psi / \partial T + \omega \langle \psi \rangle_\gamma^{-1} \partial \psi / \partial \zeta = -\psi; \quad (4.16)$$

$$\psi|_{T=0} = \psi_0(\zeta, \infty), \quad \psi|_{\zeta=0} = B[\varepsilon \omega / \langle \psi \rangle_\gamma]^n. \quad (4.17)$$

As before, for the distribution function we obtain

$$\psi^*(\zeta, T) = \exp(-T) \psi_0[\zeta - \lambda(T)] H[\zeta - \lambda(T)] + \\ + B \varepsilon^n \int_0^T [C(x)]^n \delta[\zeta - \lambda(T) + \lambda(x)] \exp(x) dx. \quad (4.18)$$

The moment of the order of γ is of fundamental importance for closing the problem:

$$\langle \psi \rangle_\gamma = \exp(-T) \left\{ \int_0^\infty [\zeta + \lambda(T)]^\gamma \psi_0(\zeta, \infty) d\zeta + \right. \\ \left. + B \varepsilon^n \int_0^T [C(x)]^\gamma [\lambda(T) - \lambda(x)]^\gamma \exp(x) dx \right\}. \quad (4.19)$$

Other moments are also found from (4.19) by replacing γ with the appropriate index.

Equation (4.19), combined with Eqs. (4.5) and (4.8) (or (4.10)), is the main equation of the problem. We note that if (4.5) and (4.8) are used, (4.19) can be written as one equation for determining the function $\lambda(T)$. Once this function is found, the solution is given by Eq. (4.18) and any moment of interest, by (4.19) (when j is substituted for γ).

It is important to note that a moment of the order of $\gamma + 1$ in ζ , i.e., the third moment (according to (3.2)) in z can be determined from Eqs. (4.16) and (4.17), without solving the system (4.19), (4.3), (4.8). Indeed, multiplying (4.16) by $\zeta^{1+\gamma}$ and integrating over ζ between the limits $(0, \infty)$, we obtain

$$d \langle \psi \rangle_{1+\gamma} / dT = \omega(\gamma + 1) - \langle \psi \rangle_{1+\gamma},$$

which upon integration gives

$$\langle \psi \rangle_{1+\gamma} = \omega(\gamma + 1) + [\langle \psi_0(\zeta, \infty) \rangle_{1+\gamma} - \omega(\gamma + 1)] \exp(-T).$$

This is of special practical interest since the third moment of the function f is proportional to the total volume of the crystals. Sometimes only this value need be known.

Equation (4.19) simplifies appreciably for integral γ . We shall show that in this case the solution of the problem as a whole reduces to integration of a nonlinear system of ordinary differential equations for moments. The number of crystals is determined by an equation obtained by integrating (4.16) over ζ between the limits $(0, \infty)$:

$$d \langle \psi \rangle_0 / dT = B \varepsilon^n \omega^{n+1} / \langle \psi \rangle_\gamma^{n+1}. \quad (4.20)$$

It is readily seen that moments with indices differing by unity are linked by the differential relation

$$d \langle \psi \rangle_k / dT = \omega k \langle \psi \rangle_\gamma^{-1} \langle \psi \rangle_{k-1} - \langle \psi \rangle_k, \quad k \geq 1, \quad (4.21)$$

i.e., for integral γ , starting from Eq. (4.21) for $k = \gamma$, we successively go over to the equation with $k = \gamma - 1$, etc., up to $k = 1$. These k equations, together with (4.20), form a closed system, the initial conditions for which are obtained by calculating the respective moments of $\psi_0(\zeta, \infty)$ (4.17). After integrating the given system, from (4.5) we find the supersaturation and the parameter λ appearing in the computational formulas is determined by simple quadrature of (4.8).

5. The Stability of the Stationary Solution. Since it is known [10-12, 14] that crystallization can occur in a self-oscillating mode, whether the stationary solution of (3.3), (3.5) is stable is an open question. In the given case, since we used the limiting simplification $\varepsilon \rightarrow 0$ on passing from (3.4) to (3.5), it will be a question of transient perturbations with a characteristic time τ_1 , i.e., a question of the stability of the stationary solution of the problem (4.16), (4.17).

We substitute $\psi = \psi_\infty(\zeta) + \hat{\psi}(\zeta) \exp(pT)$ into Eq. (4.16) and the boundary condition (4.17). Assuming that the perturbation of the solution ψ is small in comparison with ψ_∞ , we linearize the resulting equation in the neighborhood of ψ_∞ . To determine the perturbation $\hat{\psi}$ we have the problem

$$p \hat{\psi} + \frac{\omega}{\langle \psi_\infty \rangle_\gamma} \frac{d \hat{\psi}}{d \zeta} - \frac{\omega \langle \hat{\psi} \rangle_\gamma}{\langle \psi_\infty \rangle_\gamma^2} \frac{d \psi_\infty}{d \zeta} = \hat{\psi}, \quad \hat{\psi} |_{\zeta=0} = \frac{B n (\omega \varepsilon)^n}{\langle \psi_\infty \rangle_\gamma^{n+1}} \langle \hat{\psi} \rangle_\gamma.$$

After straightforward but long manipulations, we arrive at an equation for finding the frequency parameter p :

$$(p + 1)^{\gamma+2} + np = 1. \quad (5.1)$$

Clearly, one of the roots of (5.1) is the point $p = 0$. It lies on the boundary of the region of stability and does not depend on γ and n . The solution may lose stability at that point because a second-order root of (5.1) appears at it, which happens for $\gamma + 2 + n = 0$. This equality does not hold for the usual practical values $\gamma > 0$, $n > 0$, but functions describing nucleation due to the Tammann effect [14, 20] are nevertheless of interest for descending branches ($n < 0$). For integral values of γ Eq. (5.1) is a classical problem of determining the roots of a polynomial. A number of theorems and general methods [21], often not requiring calculation of the roots of the polynomial, are available for problems of analysis of the position of these roots in the plane p , which is important for the problem of the stability of the stationary solution.

In the more general situation to determine the boundary of the region of stability we substitute $p = i\nu$, where ν is real, into (5.1) and separate the real and imaginary parts of the resulting expression. As a result, we have two relations ($\varphi = \arctan \nu$):

$$\cos [(\gamma + 2) \varphi] = \cos^{\gamma+2} \varphi, \quad n \operatorname{tg} \varphi + \operatorname{tg} [(\gamma + 2) \varphi] = 0. \quad (5.2)$$

Since the coefficients in (5.1) are real and as a result Eqs. (5.2) are asymmetric under a change in sign of φ , it is sufficient to consider the intervals $\nu \geq 0$ or $\varphi \in (0, \pi/2)$.

Depending on the value of γ , Eqs. (5.2) give several branches which divide the entire (γ, n) plane into alternating regions of stability and instability of the stationary solution. The physical value has a rather limited number of them. This is because γ and n are positive and vary within limited intervals. In most studies on this subject these parameters lie within the ranges $\gamma \in (0, 5)$, $n \in (0, 15)$, although there are variants where $\alpha \rightarrow -1$, i.e., $\gamma \rightarrow \infty$.

The branch, having at $\gamma = 1$ vertical asymptote line is of particular interest (Fig. 2, curve 1). Naturally, this pertains only to branches of the first quadrant of the (γ, n) . For purposes of demonstration Fig. 2 shows one more branch (line 2), which exists for $\gamma > 5$ ($\gamma = 5$ is its vertical asymptote). It lies in the region of values of the parameters that are fairly high from the standpoint of applications. In our problem its value is evidently low. In other such problems in this field it may turn out that a similar branch should be taken into account during analysis of the stability of the system.

Curves 1 and 2 divide the first quadrant of the (γ, n) plane into regions of stability I and III and a region of instability II. Other curves, determining the lines of change of stability, go beyond the limits of Fig. 2. We note that the exponent n on

the first line of Fig. 2 has the asymptotic value $n \cong (36/\pi^2)/(\gamma - 1)^2$ as $\gamma \rightarrow 1$ and $n \cong \gamma^{1/2}$ as $\gamma \rightarrow \infty$. The latter asymptotic equation is appropriate for calculations when γ is of the order of several hundred, i.e., of little use in practice. The exponent n increases slightly in the range of γ in Fig. 2.

Figure 3 shows the graphs of the variable φ , related to ν as $\nu = \tan \varphi$. The numbers of the curves in Fig. 3 correspond to branches 1 and 2 in Fig. 2. These curves make it possible to determine the frequency of self-oscillations when they appear.

REFERENCES

1. R. I. Nigmatulin, *Fundamentals of the Mechanics of Heterogeneous Media* [in Russian], Nauka, Moscow (1978).
2. I. N. Dorokhov, V. V. Kafarov, and E. M. Kol'tsova, "Equations of thermal fluid mechanics of a two-phase polydisperse medium with phase transitions and a continuous size distribution of particles," *Prikl. Mekh. Tekh. Fiz.*, No. 1 (1978).
3. I. N. Dorokhov, V. V. Kafarov, and E. M. Kol'tsova, "Equations of thermal fluid mechanics for describing processes of mass crystallization from solutions and the vapor phase," *Prikl. Mekh. Tekh. Fiz.*, No. 6 (1981).
4. M. V. Buikov, "Evaporation of polydisperse fog," *Kolloidn. Zh.*, **24**, No. 4 (1962).
5. Yu. A. Buevich, "Kinetics of mass exchange of a polydisperse system of particles with the ambient medium," *Prikl. Mekh. Tekh. Fiz.*, No. 1 (1966).
6. A. Ya. Lukin and A. M. Stepanov, "Dynamics of aerosol formation from supersaturated vapor," *Prikl. Mekh. Tekh. Fiz.*, No. 3 (1984).
7. A. A. Moshinskii and M. I. Sibirev, "Mass crystallization with allowance for pulsation of the crystal growth rate," *Prikl. Mekh. Tekh. Fiz.*, No. 6 (1984).
8. I. B. Berliner, "Kinetics of the crystallization of salts from supersaturated solutions," *Zh. Fiz. Khim.*, **48**, No. 3 (1974).
9. A. A. Moshinskii, "Some cases of crystallization of salts from solutions," *Teor. Osn. Khim. Tekhnol.*, **18**, No. 4 (1984).
10. S. J. Lie, R. Shinnar, and S. Katz, "The stability and dynamic behavior of a continuous crystallizer with a fines trap," *AIChE J.*, **17**, No. 6 (1971).
11. B. Anshus and E. Ruckstein, "On the stability of a well stirred isothermal crystallizer," *Chem. Eng. Sci.*, **28**, No. 2 (1973).
12. L. B. Berliner and V. M. Gorin, "Study of the dynamics of a continuous isothermal crystallizer," *Teor. Osn. Khim. Tekhnol.*, **7**, No. 5 (1973).
13. Yu. A. Buevich and V. V. Mansurov, "Contribution to the theory of shock boiling," *Inzh. Fiz. Zh.*, **47**, No. 6 (1985).
14. Yu. A. Buevich, V. V. Mansurov, and I. A. Natalukha, "Weakly nonlinear self-oscillations during bulk crystallization," *Inzh. Fiz. Zh.*, **49**, No. 2 (1985).
15. N. I. Litunovskii and O. M. Todes, "Kinetic growth of crystals in a region limited by the molecular diffusion rate," *Zh. Tekh. Fiz.*, **23**, No. 7 (1953).
16. A. A. Chernov, E. I. Givargizov, Kh. S. Bagdasarov, et al., *Modern Crystallography, Vol. 3, Formation of Crystals* [in Russian], Nauka, Moscow (1980).
17. J. Cowl, *Perturbation Methods in Applied Mathematics* [Russian translation], Mir, Moscow (1972).
18. O. M. Todes, V. A. Seballo, and A. D. Gol'tsiker, *Mass Crystallization from Solutions* [in Russian], Khimiya, Leningrad (1984).
19. S. K. Godunov, *Equations of Mathematical Physics* [in Russian], Nauka, Moscow (1971).
20. B. I. Kidiyarov, *Kinetics of Liquid-Phase Crystallization* [in Russian], Nauka, Novosibirsk (1979).
21. M. A. Lavrent'ev and B. V. Shabat, *Methods of the Theory of Functions of Complex Variables* [in Russian], Nauka, Moscow (1973).