ANALYSIS OF THE LIMITING REGIME OF A CONTINUOUS PROCESS OF MASS CRYSTALLIZATION OF SALTS FROM SOLUTIONS

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Crystallization of a polydisperse system of crystals with continuous organization of the process is investigated. The statement of the problem includes two characteristic time scales: the time of transfer of particles through a crystallizer and the "growth" time of the crystals. A variant where the first time is substantially larger than the second one is analyzed. Expansions useful for describing the process with each of the above time scales are constructed by a small-parameter method.

Introduction. The process of mass crystallization of salts from solutions is described in a manner exhaustive for practical needs, using the function of size distribution of crystals F. Knowledge of this function makes it possible to trace the time variation of such characteristics of a polydisperse system as the number of particles, their average size, the total volume of crystals in the system. A characteristic feature of equations for the process of mass crystallization is their nonlinearity, which is mainly the reason for the relatively small number of exact solutions obtained for these equations, and even then basically for a periodic process. For a continuous process it is the stationary solutions that are easiest to determine. In this case the equations of the problem are transformed into ordinary differential ones (the original equations were in partial derivatives), and the nonlinearity manifests itself in an algebraic manner: it reduces to the solution of a transcendental equation. The process in the regime of ideal mixing is dealt with here. Nonstationary problems are much more intricate. In this case one is usually interested in how the process reaches the stationary regime (transient process) as well as in the stability of the stationary regime and the related development of self-excited oscillations. The intricacy of problems of nonstationary mass crystallization enables us to consider reduction of the problem to a system of ordinary differential equations or to integrodifferential equations of a simple form to be a certain achievement since it often turns out that it is much easier to investigate these equations than the original ones. The idea of special features of the analysis of equations for mass continuous crystallization and the approaches applied there can be gained, for example, from [1-6]. We note that as concerns the methods of investigation the process of crystallization is similar to that of mass dissolutional, though there are certain differences in the statement of additional conditions, and so on.

Here using small parameter methods [7, 8] we will construct asymptotic solutions of the equations of continuous crystallization in one limiting variant.

Statement of the Problem. We will take the basic equations of the problem in the form

$$\partial F/\partial \tau + U\hat{C}\partial (F/r^{\alpha})/\partial r = [F_*(r, \tau) - F(r, \tau)]/\tau_1, \tag{1}$$

$$d\hat{C}/d\tau = -\beta U\hat{C} \int_0^{\infty} r^{2-\alpha} F(r, \tau)\, dr + \varkappa(\hat{C}_* - \hat{C})/\tau_1, \tag{2}$$

where the rate of crystal growth is taken to depend on the supersaturation $\hat{C}$ and the crystal size r by the formula $V = U\hat{C}/r^{\alpha}$. Here U and α are constants. We assume that from the concentration of the dissolved solid phase an equilibrium portion is subtracted, and thus the total supersaturation release corresponds to $\hat{C} = 0$. A similar law for various α is usually encountered in practice. A more intricate dependence on $\hat{C} - \varphi(\hat{C})$, $\varphi(0) = 0$ (one often takes $\varphi(\hat{C}) = U\hat{C}^k$, k = const) — creates no principal complications. The parameter τ_1 expresses the characteristic time of transfer of the crystals through an apparatus. It is equal to the ratio of the crystallizer volume to the volume flow rate of the solid phase. Trans-

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fer of the solute may occur, generally speaking, with another rate. This circumstance is taken into account by the parameter $\varkappa$, equal to the ratio of the flow rate of the target substance in the solution to the flow rate of the substance in the crystals. The constant β characterizes the shape of the crystals, their density, etc. In general this parameter is to be prescribed such that it correctly describes the rate of transition of the substance from the solution to the solid phase, which is determined by the second term in Eq. (2). The first term in this equation describes the variation in the concentration of the substance in the solution, and the third one describes transfer of the substance through the crystallizer with allowance for the incoming flow with the target component concentration $\hat{C}_*$, which will be considered constant. The terms in Eq. (1) determine a variation of the distribution function $(\partial F/\partial \tau)$ caused by crystal growth (the second term) and crystal transfer in intensive mixing (the third one). The derivation of the system (1), (2) from a more general one, taking into account longitudinal mixing in the continuous and dispersed phases and a more detailed discussion of some parameters, is given in [6]. In particular, here we take no account of the influence of fluctuations of the crystal growth rate on the process.

Equations (1) and (2) supplement the initial and boundary conditions:

$$F|_{\tau=0} = F^0(r), \quad \hat{C}|_{\tau=0} = C^0, \quad F/r^\alpha|_{r=0} = J\hat{C}^m/(U\hat{C}), \tag{3}$$

where $J\hat{C}^m$ is the nucleation intensity (J and m are constants). Here we have taken a power form of the law for the intensity of formation of a new phase, which is often used in practice. We introduce the dimensionless variables and parameters:

$$f = F\beta\rho^4/C^0, \quad f^0 = F^0\beta\rho^4/C^0, \quad C = \hat{C}/C^0, \quad C_* = \hat{C}_*/C^0, \quad z = r/\rho,$$
$$\tau_2 = \rho^{\alpha+1}/UC^0, \quad t = \tau/\tau_2, \quad \varepsilon = \tau_2/\tau_1, \quad f_*(z, t) = F_*(r, \tau)\beta\rho^4/C^0, \tag{4}$$

where ρ is the scale for the crystal size, which can be determined, for example, from the character of variation of the initial distribution function $F^0(r)$. In the variables of (4) problem (1)-(3) is written as

$$\partial f/\partial t + C\partial (f/z^\alpha)/\partial z = \varepsilon [f_*(z, t) - f(z, t)], \tag{5}$$

$$dC/dt = -C \int_0^\infty z^{2-\alpha} f(z, t)\, dz + \varepsilon\varkappa (C_* - C), \tag{6}$$

$$f|_{t=0} = f^0(z), \quad C|_{t=0} = 1, \quad f/z^\alpha|_{z=0} = BC^n, \tag{7}$$

where $B = J\beta\rho^{\alpha+4}(\hat{C}^0)^{m-2}/U$, $n = m - 1$. We point out that it would be possible to choose the scale ρ for the crystal size by setting B equal to unity.

Relations (4) show that problem (1)-(3) contains two characteristic times τ_1 and τ_2. Depending on the relation of these scales these or other terms will prevail in certain time scales. Here we will consider the variant $\epsilon \ll 1$ and will construct the solution of problem (5)-(7) using a perturbation method [7, 8].

External Solution. We seek a solution of the problem in the form of the series

$$f(z, t) = f_0(z, t) + \varepsilon f_1(z, t) + ..., \quad C(t) = C_0(t) + \varepsilon C_1(t) + ..., \tag{8}$$

on substitution of which into relations (5)-(7) with separation of terms of the same order with respect to ϵ we arrive in the main approximation with respect to ϵ at the problem

$$\partial f_0/\partial t + C_0\partial (f_0/z^\alpha)/\partial z = 0, \tag{9}$$

$$dC_0/dt = -C_0 \int_0^\infty z^{2-\alpha} f_0(z, t)\, dz, \tag{10}$$

$$f_0|_{t=0} = f^0(z), \quad C_0|_{t=0} = 1, \quad f_0/z^\alpha|_{z=0} = BC_0^n. \tag{11}$$

Let us introduce the moment characteristics of the function f_0 (and similarly of other functions) by the formula

$$\langle f_0 \rangle_j = \int_0^\infty z^j f_0(z, t)\, dz. \tag{12}$$

We multiply Eq. (9) by z^3, integrate over z within the limits $(0, \infty)$, and add to the result Eq. (10) multiplied by a factor of three. In the final analysis we obtain

$$d(3C_0 + \langle f_0 \rangle_3)/dt = 0. \tag{13}$$

Integrating Eq. (13) yields

$$3C_0 + \langle f_0 \rangle_3 = 3 + \langle f^0 \rangle_3 = \text{const.} \tag{14}$$

The main approximation with respect to ϵ of problem (5)-(7) — system (9), (11), and (14) — is a characteristic problem of periodic mass crystallization, which (with different values of the parameters) has been repeatedly (see, for example, [9-14]) dealt with in the literature. In a somewhat more general statement this problem was investigated in [15, 16], where some exact solutions were obtained. The work [17] proposes an approximate algorithm of the solution to problem (9), (11), and (14), giving an exactness fully acceptable in practice. Thus we regard the solution of the given problem (i.e., the function f_0 and others) as well known.

We note some facts established earlier [15]. The solution of the problem, i.e., the function $f_0(z, t)$, as i $\to \infty$ tends to an equilibrium value, which will be denoted by $f_0(z, \infty)$, with C_0 tending to zero. As for the function C, it does not attain zero and tends to some constant, being of first order with respect to the small parameter ϵ. The distribution function f has f_0 as its "intermediate" limit. Once the solution has reached $f_0(z, \infty)$, a slower evolution of the distribution function with the characteristic time τ_1 begins, or, according to the terminology of [7, 8], changes occur in the system with an "internal time" $T = \tau/\tau_1 = \epsilon t$. Thus, we are led to the need for constructing the "internal" expansion to more completely describe the solution of the problem. It is noteworthy that in this paragraph we assumed the function f_* to be of the order of unity with respect to the small parameter ϵ. We will subsequently hold to this assumption. Otherwise constructing the "internal" expansion will change slightly.

Internal Solution. We write in the internal variables the equations of the problem as

$$\partial f/\partial T + (C/\epsilon)\,\partial (f/z^\alpha)/\partial z = f_*(z, T) - f(z, T), \tag{15}$$

$$dC/dT = -(C/\epsilon) \int_0^\infty z^{2-\alpha} f(z, T)\,dz + \varkappa(C_* - C). \tag{16}$$

Since the function f_* does not appear in the main approximation of the external solution, we will subsequently consider τ_1 to be the scale of its variation, which corresponds to the description of Eq. (15). The limiting values of f_0 and C_0, as t $\to \infty$, as well as the form of Eqs. (15) and (16) make it possible to choose the internal expansion in the following manner:

$$\bar{f}(z, T) = \bar{f}_0(z, T) + \mu(\epsilon)\bar{f}_1(z, T) + ...,$$
$$\bar{C}(T) = \epsilon\bar{C}_0(T) + \nu(\epsilon)\bar{C}_1(T) + ..., \tag{17}$$

whose substitution into (15) and (16) with separation of the main terms yields the equations [$\mu(\epsilon) \to 0$, $\nu(\epsilon)/\epsilon \to 0$ for $\epsilon \to 0$]:

$$\partial \bar{f}_0/\partial T + \bar{C}_0\,\partial (\bar{f}_0/z^\alpha)/\partial z = f_*(z, T) - \bar{f}_0(z, T), \tag{18}$$

$$\bar{C}_0(T) \int_0^\infty z^{2-\alpha}\bar{f}_0(z, T)\,dz = \varkappa C_* = \bar{C}_0(T) \langle \bar{f}_0 \rangle_{2-\alpha}. \tag{19}$$

where with the overscore we denote the sought values of the internal expansion. We will subsequently assume that $C_* \neq 0$; otherwise the problem will be noticeably simplified since we will obtain $C_0 = 0$, and Eq. (18) will essentially become an ordinary differential one.

Equation (16) has acquired the "stationary" form (19) in the main approximation, and therefore for C_0 no initial condition is needed. The additional conditions for Eq. (18) obtained using the procedure of limiting joining [7, 8] become

$$\bar{f}_0|_{T=0} = f_0(z, \infty), \quad \bar{f}_0/z^\alpha|_{z=0} = 0. \tag{20}$$

When deriving boundary condition (20) we consider that in boundary condition (7) n > 0, which is usually encountered in practice. It is the structure of boundary condition (7) that makes it possible to determine the form of the functions $\mu(\epsilon)$ and $v(\epsilon)$ in (17). However, here we will confine ourselves to the terms of the basic approximation as earlier in the external solution.

The moment characteristics of the process are of certain interest since they are proportional to the integral variables: the total volume of the crystals, the number of crystals, etc. To calculate the zero moment, we will derive the corresponding equation, for the purpose of which we integrate Eq. (18) over z between the limits $(0, \infty)$. In view of (20) we obtain the equation

$$d \langle \bar{f}_0 \rangle_0 / dT = \langle f_* \rangle_0 - \langle \bar{f}_0 \rangle_0, \tag{21}$$

whose integration yields the complete kinetics of variation in the total number of crystals in the internal solution:

$$\langle \bar{f}_0 \rangle_0 = \langle f_* \rangle_0 + [\langle f_0(z, \infty) \rangle_0 - \langle f_* \rangle_0] \exp(-T). \tag{22}$$

In integrating (21), for simplicity of writing the expressions we assumed $f_* = \text{const}(T)$ and hence $\langle f_* \rangle_0 = \text{const}(T)$. The same will be assumed subsequently in solving the moment equations. In a similar way we derive the equation for the third moment, which is proportional to the total volume of the crystal:

$$d \langle \bar{f}_0 \rangle_3 / dT = \langle f_* \rangle_3 + 3 \varkappa C_* - \langle \bar{f}_0 \rangle_3. \tag{23}$$

The solution of Eq. (23) is analogous to (22):

$$\langle \bar{f}_0 \rangle_3 = [\langle f_* \rangle_3 + 3 \varkappa C_*][1 - \exp(-T)] + \langle f_0(z, \infty) \rangle_3 \exp(-T). \tag{24}$$

We will give one more useful equation for the moment characteristics. We multiply (18) by $z^{2-\alpha}$ ($\alpha \leq 2$) and integrate over z between the limits $(0, \infty)$. As a result, taking (19) into account, we find

$$d \langle \bar{f}_0 \rangle_{2-\alpha} / dT = \langle f_* \rangle_{2-\alpha} - \langle \bar{f}_0 \rangle_{2-\alpha} + [\varkappa C_*(2-\alpha)] \langle \bar{f}_0 \rangle_{1-2\alpha} / \langle \bar{f}_0 \rangle_{2-\alpha}. \tag{25}$$

With $\alpha = 2$ and $\alpha = -1$ we come to the known equations (21) and (23), applicable in a wide range of variation of α. With $\alpha = 1/2$ we obtain a new equation for the moment $\langle f_0 \rangle_{3/2}$. The zero moment, entering in (25) with $\alpha = 1/2$, should be considered known (expression (22)). The case $\alpha = 1/2$ is of certain practical interest, since it is realized in crystallizers at Reynolds numbers exceeding 500 [18]. Making use of (19), the equation for the supersaturation C_0 can be written instead of (25). Once the function C_0 is found, the problem of determining the distribution function from Eq. (18) becomes linear, whose solution is easily found, for example, by the method of characteristics. We note that the problem of continuous crystallization with $\alpha = 1/2$ may be reduced to a system of ordinary differential equations for the moments, without assumption of the smallness of the parameter ϵ (see [6]). With $\alpha = 2$ together with the kinetics of the number of crystals (22) we also obtain, as follows from (19), the law of time variation of the supersaturation C_0 and hence, once Eq. (18), which is linear now, is solved, the distribution function f_0. The given law for the growth rate was used in [12] and other works in periodic organization of the process, and in the same manner as for the variant $\alpha = 1/2$, it reduces to the "moment" system [6] in a more general case. In yet another variant of the kinetic regime $\alpha = 0$, which is important in practice, Eq. (25) can be used, since it gives the relation between the second and first moments. Obtaining in the usual way the equation for the first moment

$$d \langle \bar{f}_0 \rangle_1 / dT = \langle f_* \rangle_1 - \langle \bar{f}_0 \rangle_1 + (\varkappa C_*) \langle \bar{f}_0 \rangle_0 / \langle \bar{f}_0 \rangle_2 \tag{26}$$

and finding the kinetics of the zero moment (22), we in essence have arrived at a closed system of equations ((25) with $\alpha = 0$ and (26)) for determining the first and second moments and hence the supersaturation, taking into account (19) with $\alpha = 0$. Usually in the kinetic regime one has to consider a larger number of ordinary differential equations for the moments [3, 5, 9, 11, 12].

Reduction of Problem (18)-(20) to an Integrodifferential System of Equations. Construction of various expressions of the given item is useful for practical purposes if the kinetic dependences found are deficient and a more detailed description of the process is required, i.e., formation of the function of size distribution of the crystals. Direct numerical integration of nonlinear system (18), (19) is not always convenient and does not yield the analytical structure of the sought solution.
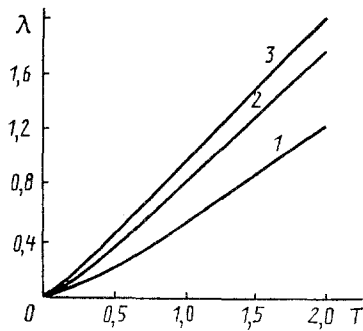
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Fig. 1

Fig. 2

Fig. 1. Solution of Eq. (33) with 1) $\alpha = 0$; 2) 0.5; 3) 1.
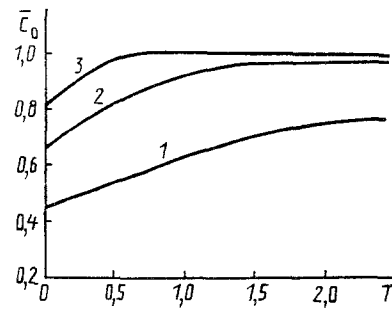
Fig. 2. Kinetics of supersaturation in the internal solution: 1) $\alpha = 0$; 2) 0.5; 3) 1.

Following [6, 15, 19], we introduce the new variables

$$\psi = \overline{f}_0/z^\alpha, \quad \zeta = z^{\alpha+1}/(\alpha + 1), \quad d\lambda/dT = \overline{C}_0, \quad \lambda|_{T=0} = 0, \tag{27}$$

in which Eq. (18) becomes

$$\partial\psi/\partial T + (d\lambda/dT)\,\partial\psi/\partial\zeta = \psi_* - \psi, \tag{28}$$

where $\psi_*(\xi, T) = f_*/z^\alpha$, and the additional conditions take the form

$$\psi|_{T=0} = g(\zeta) = f_0(z, \infty)/z^\alpha, \quad \psi|_{\zeta=0} = 0. \tag{29}$$

Here the variable z is to be expressed in terms of ξ according to (27). Between the moments of the function ψ with respect to the variable ξ and the moments of the function f_0 with respect to the variable z the relation

$$\langle \overline{f}_0 \rangle_j = (\alpha + 1)^{j/(\alpha+1)} \langle \psi \rangle_{j/(\alpha+1)}. \tag{30}$$

is easily established [6]. Applying the Laplace transform with respect to the variable ξ to Eq. (28), after some calculations we arrive at the expression for the function ψ

$$\psi(\zeta, T) = \exp(-T)\left\{ g[\zeta - \lambda(T)]\, H[\zeta - \lambda(T)] + \int_0^T \psi_* \{[\zeta - \lambda(T) + \right.$$
$$\left. + \lambda(x)],\, x\}\, H[\zeta - \lambda(T) + \lambda(x)]\exp(x)\,dx \right\}, \quad H(z) = \begin{cases} 1, & z > 0, \\ 0, & z < 0, \end{cases} \tag{31}$$

where H(z) is the Heaviside function. From here it is easy to find the moments of the function ψ:

$$\langle \psi \rangle_j = \exp(-T)\left\{ \int_0^\infty [\zeta + \lambda(T)]^j\, g(\zeta)\,d\zeta + \int_0^T \exp(x)\,dx \int_0^\infty [y + \lambda(T) - \lambda(x)]^j\, \psi_*(y, x)\,dy \right\}. \tag{32}$$

Now, making use of relation (19) and the determination of the parameter λ of (27), we substitute $j = \gamma = (2 - \alpha)/(1 + \alpha)$ into (32). Thereafter we obtain

$$[\varkappa C_*/(1 + \alpha)^\nu]\exp(T)\,dT/d\lambda = \int_0^\infty [\zeta + \lambda(T)]^\nu\, g(\zeta)\,d\zeta + \int_0^T \exp(x)\,dx \int_0^\infty [y + \lambda(T) - \lambda(x)]^\nu\, \psi_*(y, x)\,dy \tag{33}$$

— the basic integrodifferential equation of the problem.

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Indeed, solving Eq. (33), i.e., obtaining the function $\lambda = \lambda(T)$, we will determine the distribution function by expression (31) and any moment thereof by (32). The kinetics of supersaturation is found either by differentiating this function according to (27) or from relation (19) with the aid of the moment of order γ. We point out that with positive integer values of γ Eq. (33) may be reduced to an ordinary differential one.

Figure 1 presents some examples of a numerical solution of Eq. (33). The kinetics of supersaturation corresponding to these solutions is shown in Fig. 2. It is assumed that a zero-size monodisperse fraction is supplied to the crystallizer inlet, i.e., $\psi_*(\xi, T) = \psi_*\delta(\xi)$ ($\psi_* = $ const), and the initial distribution function of the internal solution $g(\xi)$ also expresses a monodisperse composition, which occurs in the complete process (including the external solution) with a monodisperse seed and negligible influence of nucleation [B $\to$ 0 in (7)].

In the example use was made of the value of the dimensionless crystal radius, equal to 1.5, i.e., the function $g(\xi) = g\delta(\xi - 1.5)$ ($g = $ const). It is easily seen that the same degree of monodispersion will also be found in the variables (z, f) without emergence of additional multipliers. In the calculations use was made of the following normalization: $\psi_* = g = \varkappa C_*/(1 + \alpha)^\gamma$.

The lines $\lambda(T)$ in Fig. 1 are fairly close to straight lines, which may be used to construct approximate solutions. We note that such an approximation was in essence applied in [1, 2] and other works by the same authors in deriving the basic evolutionary equation of crystallization etc. The data of Fig. 1 confirm to some extent the admissibility of a similar approach.

The curves in Fig. 2 asymptotically attain stationary values of supersaturation, which are obtained below (see formula (38)). This served as a check for accuracy of the calculation. It should be remembered that only the "internal" value of supersaturation is presented, without the factor ϵ. A general pattern of the variation of supersaturation in the given example is derived from its (asymptotic) decrease to zero in the zero approximation, with respect to ϵ, of the external solution and the evolution of the order of ϵ, as a first approximation and at large values of the time (transition to the internal solution with the time scale τ_1), of supersaturation growth at the expense of the "source" C_*. It is the latter that is characterized by the curves in Fig. 2.

Stationary Solution. Let the function f_* and hence ψ_k be independent of time. Then from (31)-(33) by the limiting transition $T \to \infty$ the stationary solution $\psi = \psi_\infty(\xi)$ can be obtained with certain assumptions. However, it is easier to directly integrate the stationary equation (28) in view of the fact that $\partial\lambda/\partial T = C_0 = $ const. Using boundary condition (29) we have

$$\psi_\infty(\zeta) = \exp(-\zeta/\bar{C}_0) \int_0^\zeta \psi_*(\zeta) \exp(\zeta/\bar{C}_0)\, d\zeta/\bar{C}_0. \tag{34}$$

Calculating the moment of the function $\psi_\infty(\xi)$ of order γ and substituting the result into (19), we arrive at the following equation for determining the equilibrium value of supersaturation:

$$\omega = \varkappa C_*/(1 + \alpha)^\gamma = \int_0^\infty \psi_*(\zeta) \exp(\zeta/\bar{C}_0)\, d\zeta \int_\zeta^\infty \eta^\gamma \exp(-\eta/\bar{C}_0)\, d\eta. \tag{35}$$

Under the condition of the problem ω and C_0 as well as the function ψ_* cannot be negative. It is easily seen in this case that ω as a function of C_0 will be monotonically increasing (for example, it can be checked that $\omega'(C_0) > 0$). It is also not difficult, replacing η^γ by its value at the lower limit of internal integral (35), to obtain the estimate

$$\omega > \bar{C}_0 \langle \psi_* \rangle_\gamma, \quad \bar{C}_0 > 0, \tag{36}$$

from which it follows that ω also tends to infinity with indefinitely increasing C_0. As $C_0 \to 0$ for functions ψ_* of a certain class by the saddle-point method we obtain the asymptotic expression

$$\omega \cong \bar{C}_0 \langle \psi_* \rangle_\gamma, \quad \bar{C}_0 \to 0, \tag{37}$$

which was to be expected on the basis of stationary equation (15) as $C_0 \to 0$. Relation (37) makes it possible to replace strict inequality (36) by a nonstrict one and to establish that the interval of the variable $C_0 \in (0, \infty)$ corresponds to the interval of the function $\omega \in (0, \infty)$, and since this function is continuous and monotonic, it has the unique reciprocal $C_0 = C_0(\omega)$, i.e., Eq. (35) is uniquely solvable in relation to the sought value of the equilibrium supersaturation C_0. The data of the argument are of the "physical" level of rigor.

In particular, we did not specify the class of the functions $\psi_*(\xi)$. However, for the physically important case of continuous functions $\psi_*(\xi)$ tending rapidly enough to zero as $\xi \to \infty$ (in practice $\psi_*(\xi)$ is finite, i.e., $\psi_* = 0$ $\xi \geq \xi_m = $ const > 0), all steps of the evidence for the existence and uniqueness of the root in (35) are rigorously substantiated. Nevertheless, to simplify calculations, generalized functions are often used in applications. In the given problem, when the relations (36) and (37) are to be refined, $\psi_* = N\delta(\xi)$, characterizing the supply of the monodisperse system of zero-size crystals to the inlet of the apparatus, may serve as such a function ($\delta(\xi)$ is the Dirac delta-function). In this case Eqs. (34) and (35) are simplified, and the latter yields an explicit expression for the sought root:

$$\overline{C}_0 = \{\omega/[N\Gamma(1+\gamma)]\}^{1/(1+\gamma)}, \tag{38}$$

where $\Gamma(z)$ is the Euler gamma-function. One more variant — a combination of a continuous function and $\delta(\xi)$ — essentially reduces to the above-discussed cases by dividing (35) into two terms. Here it is also easy to check the existence of a unique root of Eq. (35). We will not elaborate on other examples of the analysis of the existence of roots in (35). Usually these problems are solved without difficulty with a specific definition of the function $\psi_*(\xi)$.

Crystallization with Recycling. To produce a composition of higher quality, in practice the supply of a portion of the crystals from the apparatus outlet to its inlet is used. It is usually small crystals, which have not managed to grow to the required sizes. To describe this phenomenon, the function of the inlet f_* in Eq. (5), etc., should be modified by adding the corresponding fraction of the function f to it. In this case account must be taken of the fact that the recycled particles arrive at the inlet with some delay, which in the general case may depend on the crystal size. For small particles the given dependence is apparently of little significance; therefore we assume the delay time to be identical for all crystals and equal to τ_3. Since transfer of the substance from the crystallizer outlet to the inlet is related to its transport through pipelines, etc., it is natural to assume that the time τ_3 is of order τ_1. In this case the given effect will be unimportant in the main approximation of the external solution and will solely in the internal solution, which will be considered further.

The fraction of recycled particles depends on the method of grading the particles at the outlet from the crystallizer, which may lead to different effects. We describe the given phenomenon using the function $E(z)$, which, being multiplied by $f(z, T - T_3)$, where $T_3 = \tau_3/\tau_1$, yields the value, corresponding to recycling, of the distribution function entering the system, i.e., the function $f_*(z, T)$ in (15) should be replaced by

$$E(z) f(z, T - T_3) + f_*(z, T). \tag{39}$$

Ideally, the function $E(z)$ should be a step function, expressed in terms of the Heaviside function: $E(z) = H(z_m - z)$. This indicates that all particles of size smaller than z_m will be passed through the crystallizer again. In solving the corresponding equations account must be taken of the fact that the value of the function $f(z, T - T_3)$ should be assumed equal to zero for $T < T_3$, i.e., until the first portion of recycled particles arrives at the inlet of the apparatus.

Instead of (33) the basic equation of the process will be

$$[\varkappa C_*/(1 + \alpha)^\gamma] \exp(T) dT/d\lambda = \int_0^\infty [\zeta + \lambda(T)]^\gamma g(\zeta) d\zeta + $$
$$+ \int_0^T \exp(x) dx \int_0^\infty [y + \lambda(T) - \lambda(x)]^\gamma [\psi_*(y, x) + E(y)\psi(y, x - T_3)] dy. \tag{40}$$

It should be considered together with the equation for the distribution function:

$$\psi(\zeta, T) = \exp(-T)\Big\{ g[\zeta - \lambda(T)] H[\zeta - \lambda(T)] + \int_0^T \exp(x)[\psi_*(\Phi, x) H(\Phi) + $$
$$+ E(\Phi)\psi(\Phi, x - T_3)] dx \Big\}, \quad \Phi = \zeta - \lambda(T) + \lambda(x), \tag{41}$$

which noticeably complicates the problem. No basic difficulties emerge only in analysis of the stationary solution, which, taking into account that the time argument disappears and hence the delay is not taken into account, reduces to the expression

$$\psi_\infty(\zeta) = (1/\overline{C}_0) \exp\Big\{ \Big[\int_0^\zeta E(z) dz - \zeta \Big]/\overline{C}_0 \Big\} \int_0^\zeta \psi_*(x) \exp\Big\{ \Big[\zeta - \int_0^x E(z) dz \Big]/\overline{C}_0 \Big\} dx.$$

It is also easy to generalize Eq. (35) for determining the equilibrium value of C_0.

Conclusions. The basic equations of continuous crystallization (1) and (2), given the small parameter ϵ, are solved by constructing two expansions: (8) and (17), describing the process respectively in the initial stage (for times of order τ_2) and in the region of times of order τ_1. The main approximation of the first expansion (9)-(14) was investigated earlier [9-17]. The main approximation of the second expansion is reduced to a solution of integrodifferential equation (33). Some "moment" solutions of the problem of the internal expansion (8) are found: (22) and (24), and cases of reduction of the problem for the basic approximation to a system of ordinary differential equations are stated. The stationary solution (34) is considered whose complete investigation is reduced to transcendental equation (35). It is shown that this equation has a unique solution. Generalization of the obtained relations for the presence of recycling is discussed. The obtained results can be applied to calculating the characteristics of crystallizers operating in the continuous regime.

NOTATION

C, dimensionless supersaturation of solution; C^0, initial value of supersaturation; $C_j(t)$, components of expansion of supersaturation with respect to the small parameter ϵ in the external solution; $C(T)$, supersaturation in the internal solution; C_j, components of expansion of supersaturation in the internal solution; F_*, function of size distribution of the crystals at the inlet to the crystallizer; $F^0(r)$, initial value of the distribution function; f, $f_j(z, t)$, dimensionless distribution function and components of its expansion in the external solution; f, $f_j(z, T)$, dimensionless distribution function and components of its expansion in the internal solution; $\delta(z)$, Dirac delta-function; ϵ, small parameter; τ, time; $\langle \ \rangle_j$, designation of the moment of order j.

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