UNSTEADY CRYSTALLIZATION OF POLYDISPERSE SYSTEMS IN A CASCADE OF VESSELS

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This article examines a problem concerning the kinetics of growth of a polydisperse ensemble of crystals in a cascade of vessels in the case where the supersaturatin of the crystallizing medium filling the vessels relaxes rapidly to steady-state values. An analysis is made of the reason for the establishment of a crystal-size distribution law which is close to normal in such a system.

The crystallization processes which are common in chemical engineering, metallurgy, and geology are characterized by different physical mechanisms of crystal formation and growth [1], these mechanisms leading to the establishment of a given distribution of the particles of the new phase with regard to size. One of the main factors which determines the dispersity of the product is [2] the presence of different sources of particles in the crystallizing medium. These sources are present due to processes involving heterogeneous (secondary) nucleation, agglomeration, the entry of crystals into the system from outside, etc.

Here, we will study specific laws governing the formation of the crystal-size density function during unsteady bulk crystallization from supersaturated solutions or supercooled melts with intensive mixing of the medium (to prevent the formation of temperature and concentration gradients), continuous arrival at the j-th vessel of a two-phase medium from the (j − 1)-th component of a cascade of similar vessels, and continuous extraction of finished crystals from the j-th vessel. It is just such a scheme that is used to conduct most crystallization processes. The operation of all other sources is accounted for in the corresponding kinetic equation by a certain generalized term $Q_j(\tau, r)$.

Since the number of growing crystalline inclusions present in the system is normally quite large and since their volumes are much smaller than the volume of the matrix phase, the kinetic equation [2-4] for the density function of the crystals with respect to size r in the j-th component of the cascade $f_j(\tau, r)$ and the corresponding initial and boundary conditions can be written in the form

$$\frac{\partial f_j}{\partial \tau}+\frac{\partial}{\partial r}(f_j v_j)+\frac{1}{\theta}(f_j-f_{j-1})=Q_j(\tau, r),$$
$$f_j(\tau, 0)=0;\quad f_j(0, r)=0;\quad f_0(\tau, r)=0;\quad j=1, 2, 3, \ldots \tag{1}$$

Such conditions of unambiguity are quite permissible in light of the inhomogeneity of the initial system of equations. The presence of the solid phase at the initial moment of time and the occurrence of all types of nucleation within the vessels of the cascade can alwways be taken into account in the source terms in the right sides of the equations. Since all of the components of such a cascade are usually hydrodynamically similar to one another, the kinetic coefficient β(r) in the expression for the linear rate of crystal growth $v_j(\tau, r)$ can be considered to be independent of the number j. Then, in accordance with [2, 4], we take

$$v_j(\tau, r)=dr/d\tau=\beta(r)\,\varphi\,[S_j(\tau)]. \tag{2}$$

Here, φ is a known dimensionless function describing the relative supersaturation (supercooling) of the medium. This function is connected with the density function through its initial moments, by means of the conservation equation. This makes system (1-2) essentially nonlinear. As was shown in [3-5], at j = 1 the problem in question can be reduced to a

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unique integral equation that can be studied numerically [5] or (for sufficiently long times) analytically [3, 4]. However, this equation cannot be obtained in the more general case j > 1. Our further study of the given problem will be conducted using the example of the crystallization of polydisperse systems from solutions.

In a number of cases, the time of relaxation of supersaturation τ_r to a steady value turns out to be much less than the corresponding relaxation time of the crystal-size density function. This can occur, for example, when the chemical method of creating supersaturation is employed. Here, as a result of the mixing of two or more substances accompanied by the dissolution of a third component in them, the solubility of the latter in the mixture is sharply reduced. The resulting high degree of supersaturation of the solution is quickly eliminated by the spontaneous, avalanche formation of nuclei. After a short period of time τ_r elapses from the beginning of nucleation, the delivery of feed-solution establishes a more or less stable value of supersaturation at which subsequent crystal growth occurs. The theory developed below can be applied with almost no changes to certain cases of crystallization from melts — mainly for systems which tend to remain in a supercooled metastable state for a long period of time. If the conditions for the stability of the steady-state crystallization regime are satisfied in each cell of the cascade [4], then system of kinetic equations (1)-(2) can be solved analytically for moments of time $\tau > \tau_r$. To do this, we change over to dimensionless variables:

$$t=\tau/\theta;\ x=r/r_m;\ U_j(t,\ x)=f_j(t\theta,\ \ xr_m)\,r_m V,$$
$$R_j(t,\ x)=Q_j(t\theta,\ xr_m)\,r_m\,\theta V;\ \ g(x)=\beta(xr_m)\,\theta/r_m, \tag{3}$$
$$q_j=\varphi(S_j),\ \ j=1,\ 2,\ 3,\ \ldots,$$

then proceeding to a modified crystal size and to density and source functions established by means of the formulas:

$$y=\Psi(x)=\int_0^x d\zeta/g(\zeta);\ \ V_j(t,\ y)=g(x)\exp(t)\,U_j(t,\ x);$$
$$P_j(t,\ y)=g(x)\exp(t)\,R_j(t,\ x). \tag{4}$$

Then the initial problem (1)-(2) takes the following form in the new variables (4)

$$\frac{\partial V_j}{\partial t}+q_j\frac{\partial V_j}{\partial y}-V_{j-1}=P_j(t,\ y),\ \ j=1,\ 2,\ 3,\ \ldots;$$
$$V_0(t,\ y)=0;\ \ V_j(0,\ y)=0;\ \ V_j(t,\ 0)=0. \tag{5}$$

Having made use of a two-dimensional Laplace transform [6] for the variables t and y, we write problem (5) in the form of an equivalent system of algebraic equations for the transforms of the sought functions:

$$s\overline{\overline{V}}_j(s,\ p)+q_j\,p\overline{\overline{V}}_j(s,\ p)-\overline{\overline{V}}_{j-1}(s,\ p)=\overline{\overline{P}}_j(s,\ \ p),\ j=1,\ 2,\ 3,\ \ldots$$

Having solved the resulting system by the method of mathematical induction, we find the following expression:

$$\overline{\overline{V}}_j(s,\ p)=\sum_{k=1}^{j}\frac{\overline{\overline{P}}_k(s,\ \ p)}{\prod\limits_{i=k}^{j}(s+pq_j)},\ \ \ j=1,\ 2,\ 3,\ \ldots \tag{6}$$

Decomposing each term in the sum (6) into two factors and transforming them in succession, we can use the residue theorem [7] to obtain the final solution of system (5) in the form of the sum of j convolutions of the inverse images of these factors:

$$V_j(t,\ y)=\sum_{k=1}^{j}\frac{1}{\Gamma(j-k)}\sum_{i=k}^{j}\frac{q_i^{j-k-1}}{\prod\limits_{\substack{l=k\\ l\neq i}}^{j}(q_i-q_l)}\int_0^y d\zeta\int_0^t P_k(\eta,\ \zeta)\,(t- \tag{7}$$

$$-\eta-\frac{y-\zeta}{q_i}\Bigr)^{j-k-1} H\left(t-\eta-\frac{y-\zeta}{q_i}\right) d\eta, \quad j=1,\ 2,\ 3,\ \ldots \tag{7}$$

Taking the Heaviside function from under the sign of the internal integral and returning to the initial variables (3), we can use Eqs. (4) to obtain the final expressions for the dimensionless density functions of crystal size in the form of the following integral relations

$$U_j(t,\ x)=\frac{1}{g(x)}\sum_{k=1}^{j}\frac{1}{\Gamma(j-k)}\sum_{i=k}^{j}\frac{1}{\prod\limits_{\substack{l=k\\ l\neq i}}^{j}(q_i-q_l)}\int_0^x H\Biggl[t-\frac{\Psi(x)-\Psi(\lambda)}{q_i}\Biggr]d\lambda\int_0^{t-\frac{\Psi(x)-\Psi(\lambda)}{q_i}} R_k(\eta,\ \lambda)\exp(\eta-\lambda)\,[(t-\eta)q_i+\Psi(\lambda)-\Psi(x)]^{j-k-1}\,d\eta, \quad j=1,\ 2,\ 3,\ \ldots \tag{8}$$

The convergence of the last term (with $k = j$) in the sums (7)-(8) is not obvious, since the improper integral in it diverges. However, if the function $R_k(\eta,\ \lambda)$ satisfies Hölder's inequality with regard to η in the neighborhood of the point $\eta = t - [\Psi(x) - \Psi(\lambda)]/q_k$ -- which it almost always does – then it can be shown that at $k \to j$ this term has a finite limit equal to

$$\frac{1}{g(x)}\int_0^x H\left[t-\frac{\Psi(x)-\Psi(\lambda)}{q_k}\right]\exp\left[\frac{\Psi(\lambda)-\Psi(x)}{q_k}\right]R_k\left[t-\frac{\Psi(x)-\Psi(\lambda)}{q_k},\ \lambda\right]d\lambda. \tag{9}$$

In particular, at $j = k = 1$ it coincides with the solution obtained in [5] for the case $q =$ const.

Using Eqs. (8), it is not hard to calculate all orders of the initial and central moments of the crystal-size density function in the j-th vessel of the cascade. The former determine the main parameters of production crystals: mean size, specific surface, mass concentration of the solid phase. The latter make it possible to calculate such probabilistic characteristics of the particle distribution as the variance, coefficient of variation (the ratio of the variance to the mean size of the inclusions, characterizing the narrowness of the fraction), etc. Since the function $\Psi(x)$ may be fairly complex, numerical methods of integration are usually used to calculate these quantities. These methods make it possible to find zeroth-order moments determining the numerical concentration of crystals in the vessels. The moments are found in the form of the following analytic expressions:

$$\mu_{0j}(t)=\int_0^\infty U_j(t,\ x)\,dx=\sum_{k=1}^{j}\frac{1}{(j-k)!}\int_0^\infty dx\int_0^t R_k(\eta,\ x)\exp(\eta-t)(t-\eta)^{j-k}\,d\eta, \quad j=1,\ 2,\ 3,\ \ldots \tag{10}$$

In particular, these relations reflect the obvious fact that the concentration of crystals at any moment of time is independent of the rate of their growth at previous moments and is instead completely determined by the rate of their formation in the system at these moments, i.e., by the rate of nucleation or the law governing the admission of seed particles to the vessels. It is not hard to show that Eqs. (10) satisfy the well-known [2] system of balance equations for the number of particles along with zero initial conditions. This system, appearing as follows, is obtained by integrating the initial system of kinetic equations (1) over r within the limits 0, ∞

$$\frac{d\mu_{0j}}{dt}+\mu_{0j}(t)-\mu_{0j-1}(t)=\int_0^\infty R_j(\eta,\ x)\,dx, \quad j=1,\ 2,\ 3,\ \ldots$$

The resulting solution (8) of the problem, with crystal-source functions $Q_j(\tau,\ r)$ of arbitrary form, does not have a sufficiently clear physical meaning. To simplify interpretation of the results, we will examine two special cases of this general problem which retain the essential features of the process and make it possible to discern the basic laws governing the kinetics of crystallization in a cascade of series-connected vessels.

We will assume that the only source of inclusions growing during crystallization is homogeneous nucleation. Meanwhile, without loss of generality, we will assume that the formation of nuclei occurs only in the first cell of the cascade. In this case, the number of terms in sums (6)-(8) is reduced to one. We take into consideration the assumptions made above regarding the character of the change in supersaturation, which decreases by several orders of magnitude over a short time τ_r. Then, under the condition that the nucleation process can be classed as a "rapid type of nucleation" [8], the actual distribution of the nuclei with regard to size will quickly become the equilibrium distribution, corresponding to the instantaneous values of supersaturation. Under these conditions, the concentration of critical nuclei that corresponds to each moment of time to the equilibrium concentration will almost instantaneously drop to a negligibly low value. As a result, the source term in the first kinetic equation of system (1) can be modeled by a δ-function:

$$Q_1(\tau,\ r)=\delta(\tau,\ r-r^*)N;\quad Q_j(\tau,\ r)=0,\quad j=2,\ 3,\ \ldots;$$
$$R_1(t,\ x)=\delta(t,\ x-x^*)NV;\quad R_j(t,\ x)=0. \tag{11}$$

After these expressions are inserted into solution (8), we arrive at the following result:

$$U_j(t,\ x)=\frac{VN\exp(-t)}{g(x)\Gamma(j-1)}\sum_{i=1}^{j}\frac{H\left[t-\dfrac{\Psi(x)}{q_i}\right]}{\prod\limits_{\substack{l=1\\ l\neq i}}(q_i-q_l)}[tq_i-\Psi(x)]^{j-2}. \tag{12}$$

Despite the discontinuous character of each term individually, this function as a whole has a continuous graph. The graph is shown in Fig. 1a as a series of curves at different moments of time for a crystal growth rate which is independent of crystal size ($\beta(r)=\beta_0=\text{const}$). The increasing broadening of the graph of the function $\delta(x-x^*)NV$ over time, resembling diffusional broadening, is caused by the fact that the inclusions of the new phase in processes of this type are distributed according to not just size but other parameters as well – particularly the residence time in the vessels [9]. Since they are located for different lengths of time under different conditions characterized by different degrees of supersaturation, crystals nucleated at the same moment of time $\tau=0$ reach different dimensions by the moment they arrive at the j-th vessel (the greatest dimensions obviously will not exceed q^*t, where $q^*=\max\limits_i q_i$). This fact is also reflected in the density function (12). In this case, $U_j(t,\ x)$ can be interpreted as a joint distribution describing the residence time of crystals in the first j vessels of the cascade and the dimensions of the crystals. There is no condition for normalizing this distribution to unity.

As our second example, we will examine another extreme case. We will assume that all types of nucleation are absent from all of the vessels and that crystals of the same size are fed into the cascade at a constant rate. To make this case comparable to the first example, we take the rate to be equal to r^*. Such a situation corresponds to the following source functions:

$$Q_1(\tau,\ r)=\delta(r-r^*)N/\theta;\quad Q_j(\tau,\ r)=0,\quad j=2,\ 3,\ \ldots;$$
$$R_1(t,\ x)=\delta(x-x^*)NV;\quad R_j(t,\ x)=0,\quad j=2,\ 3,\ \ldots, \tag{13}$$

and Eqs. (8) are reduced to the following form after calculation of the corresopnding formulas by using the rules of integration by parts j – 2 times

$$U_j(t,\ x)=\frac{VN}{g(x)}\sum_{i=1}^{j}\frac{q_i^{j-2}\exp(-t)}{\prod\limits_{\substack{l=1\\ l\neq i}}^{j}(q_i-q_l)}H\left[t-\frac{\Psi(x)}{q_i}\right]\left\{-\sum_{m=0}^{j-2}\frac{1}{m!}\left[t-\frac{\Psi(x)}{q_i}\right]^m+\exp\left[t-\frac{\Psi(x)}{q_i}\right]\right\},\quad j=2,\ 3,\ \ldots \tag{14}$$

It should be noted that when j = 1, limit expression (9) should be used in place of Eq. (8) to calculate the density function. With the source term (13), expression (9) takes the form

$$U_1(t,\ x)=\frac{NV}{g(x)q_1}\exp\left[-\frac{\Psi(x)}{q_1}\right]H\left[t-\frac{\Psi(x)}{q_1}\right].$$

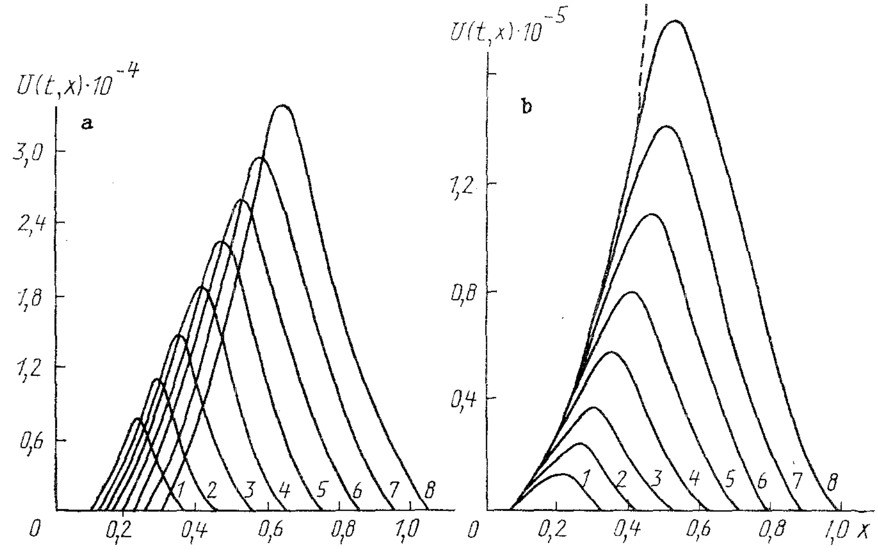

Fig. 1. Evolution of the crystal-size density function at the outlet of a five-vessel cascade with pulsed nucleation (a) in the first vessel and with a continuous input (b) of seed particles ($\beta_0 = 5.0$; $N = 1.0 \cdot 10^4$; $q_1 = 0.1$, $q_2 = 0.08$, $q_3 = 0.06$, $q_4 = 0.04$; $q_5 = 0.02$); 1) t = 0.8; 2) 1.0; 3) 1.2; 4) 1.4; 5) 1.6; 6) 1.8; 7) 2.0; 8) 2.2.

The family of curves in Fig. 1b reflects the evolution of the graph of function (14) over time.

Comparison of Fig. 1a and 1b shows that the two radically different structures of the source function (11) and (13) correspond to similar symmetric spectral functions resembling a normal distribution of a random variable. The same character of distribution evidently also exists for intermediate (in fact, for all other) source functions. Indirect proof of this can be found in the monograph [10], for example.

Let us estimate the time of relaxation of the function $U_j(t, x)$ to a stationary crystal-size distribution in each of the cases examined above. To obtain the condition of stationariness, we assume that

$$\min_{q_i} [tq_i - \Psi(x)] > 0, \tag{15}$$

Then the Heaviside function in all of the terms in Eqs. (12) and (14) can be dropped and, having used the binomial theorem, we can represent (12) as the sum of the terms which contain as factors values of the Lagrangian polynomials for the functions $(1/q)^n$ at $n = 1, 2, 3, \ldots$ at the point $1/q = 0$, where q is a continuous argument and q_i are the nodal points at which these functions are determined. Since the functions themselves are equal to zero at $1/q = 0$, then their Lagrangian polynomial also vanish at this point. Thus, Eq. (12) vanishes for all $x < x_0$, while it can readily be shown that (14) takes the form

$$U_j^*(x) = \frac{N}{g(x)} \sum_{i=1}^{j} q_i^{j-1} \frac{\exp[\Psi(x)/q_i]}{\prod\limits_{\substack{l=h \\ l \neq 1}}^{j} (q_i - q_l)}, \quad j = 2, 3, \ldots, \tag{16}$$

where we find x_0 from condition (15) in the following manner:

$$x_0 = \max_x \{\min_{q_i} [tq_i - \Psi(x)] > 0\}. \tag{17}$$

The graph of Eq. (16) is shown by the dashed line in Fig. 1.

Thus, the time over which a stationary cyrstal-size distribution (16) is established in the j-th vessel of the cascade is finite. This time is determined from condition (17) for each dimension x. If a disturbance of a stepped or pulsed nature arises at the inlet of the cascade in the steady-state regime, condition (17) allows us to evaluate the time interval necessary to establish a new steady state or to return to the initial state.

The use of more general expressions (8) and (10), corresponding to actual situations, only complicates the mathematical aspects of the problem without essentially altering the final result. If the necessary information on the rates of crystal growth (2) and formation $Q_j(\tau, r)$ is available, then by assigning different values for the supersaturation of the medium in the vessels we can calculate the corresponding crystal-size distributions at the outlet of the cascade along the crystals' numerical concentration, mean size, specific surface, etc. The mechanisms discovered in the present study make it possible to control the dispersity of production crystals and thus optimize the crystallization of polydisperse systems. For example, the methods of variational calculus can be used to minimize the width of the crystal-size distribution by establishing a suitable level of supersaturation in the vessels.

NOTATION

$f_j(\tau, r)$, density function of crystal size r in the vessel with the number j; $v_j(\tau, r)$, linear rate of crystal growth; $\beta(r)$, crystal growth rate coefficient; $S_j(\tau)$, relative supersaturation or supercooling of the medium in j-th vessel; θ, average residence time of two-phase element of the medium in the vessel; r_m, characteristic scale of crystal size; V, volume of one cell (vessel) of the cascade;' s, p, parameters of the Laplace transform; δ, λ, η, internal variables of integration; Γ, Euler gamma function; H, Heaviside function; δ, Dirac delta function; r^*, size of critical nucleus; N, initial numerical concentration of nuclei in the first volume or initial numerical concentration of crystals in forms of the corresponding functions.

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