MASS CRYSTALLIZATION WITH ALLOWANCE FOR FLUCTUATIONS OF CRYSTAL GROWTH RATE

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1. Methods for the mechanics of multiphase heterogeneous systems [1-4] are currently widely used to describe mathematically processes involved in the mass crystallization of substances for solutions and the gas phase. The method of spatial averaging [4] was used to obtain an equation for the crystal-size distribution function. One of the important characteristics of mass crystallization here is the rate of crystal growth v, which depends on the hydrodynamic situation in the reactor, the crystal size r, and the supersaturation of the carrier phase s. Three laws of crystal growth have been used most widely in practice: the kinetic regime, in which the rate v is a function only of the supersaturation, $v = \psi(s)$; the diffusive regime, in which $v = \psi(s)/r$; the growth regime $v = (a + br)\psi(s)$ (a and b are constants) [4-6]. Experimental study of the growth of fixed crystals in a supersaturated solution has shown that their growth rate fluctuates broadly for the mean [7]. Growth rate fluctuations are taken into consideration by the introduction of a diffusion term into the equation for the density of the particle-size distribution function f(t, r) [4-6]:

$$\frac{\partial f}{\partial t}+\frac{\partial (vf)}{\partial r}=\frac{\partial}{\partial r}\left(D_r\frac{\partial f}{\partial r}\right), \tag{1.1}$$

where t is time; D_r is the particle-growth-rate fluctuation factor. Equation (1.1) must be augmented by the initial and boundary conditions

$$f|_{t=0}=B(r); \tag{1.2}$$

$$-D_r\frac{\partial f}{\partial r}+vf\,|_{r=r_0}=J,\quad f\,|_{r\to\infty}\to 0, \tag{1.3}$$

which determine the initial distribution of the particles according to size B(r) and the rate of formation of new crystallization centers J. Due to the smallness of the nuclei r_0, we will assume $r_0 = 0$. It should be noted that in [4-6] nucleation is described as a volume source in the form of a Dirac delta function in the initial equation. This is essentially equivalent to boundary condition (1.3).

A common approach to solving such problems is changing over to moment equations [5, 6, 8], the more so because in practice one is often most interested in the integral characteristics of the function f(t, r) which describe the change in the mean size, surface, and mass of the crystals over time. However, direct application of the moment approach to Eq. (1.1) with a constant value of the coefficient D_r requires determination of the unknown value of f(t, 0). In the moment approach in [6], it was assumed that f(t, 0) = 0 in addition to the two natural boundary conditions (1.3). This situation can be avoided in the following manner.

2. We reduce Eq. (1.1), with conditions (1.2), (1.3), to a system of integral and differential equations generalizing the familiar Todes relations [8]. We will assume that the crystals grow in the kinetic regime and that $D_r = \text{const} \neq 0$. Having made the following substitution in problem (1.1)-(1.3)

$$\tau = D_r t,\ \varphi(s) = \psi(s)/D_r,\ J_1 = J/D_r \tag{2.1}$$

and having subjected it to a Fourier transform with the kernel $\exp(i\nu r)$, we find

$$dz/d\tau + \nu^2 z - i\nu\varphi z = J_1 + i\nu f(\tau, 0); \tag{2.2}$$

$$z\,|_{\tau=0}=\int_0^\infty B(r)\exp(i\nu r)\,dr\equiv B_1, \tag{2.3}$$

where

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$$z=\int_0^\infty f(\tau,r)\exp(ivr)\,dr,\quad i=\sqrt{-1}.$$

The solution of Eq. (2.2), with condition (2.3), has the form

$$z=\left\{B_1+\int_0^\tau (J_1+ivf(\tau,0))\exp[\nu^2\xi-ivl(\xi)]\,d\xi\right\}\exp[ivl(\tau)-\nu^2\tau], \tag{2.4}$$

where the function l is given by the equation and initial conditions

$$dl/d\tau=\varphi(s),\ l(0)=0. \tag{2.5}$$

It is easy to see that the function f is determined by the formula

$$f=\frac{1}{\pi}\,\mathrm{Real}\int_0^\infty z\exp(-i\nu r)\,d\nu. \tag{2.6}$$

Having integrated (2.6) with allowance for (2.4), we obtain an expression for the distribution function

$$\begin{aligned} f(\tau,r)=&\frac{1}{2\sqrt{\pi\tau}}\int_0^\infty B(\xi)\exp\{-[l(\tau)+\xi-r]^2/4\tau\}\,d\xi+\\ &+\frac{1}{2\sqrt{\pi}}\int_0^\tau \frac{J_1[s(\xi)]}{\sqrt{\tau-\xi}}\exp\left\{\frac{-[l(\tau)-l(\xi)-r]^2}{4(\tau-\xi)}\right\}d\xi-\\ &-\frac{1}{4\sqrt{\pi}}\int_0^\tau f(\xi,0)\frac{[l(\tau)-l(\xi)-r]}{(\tau-\xi)^{3/2}}\exp\left\{\frac{-[l(\tau)-l(\xi)-r]^2}{4(\tau-\xi)}\right\}d\xi. \end{aligned} \tag{2.7}$$

With r approaching zero in (2.7), we obtain an equation for $f(\tau,0)$:

$$\begin{aligned} f(\tau,0)=&\frac{1}{2\sqrt{\pi\tau}}\int_0^\infty B(\xi)\exp\{-[l(\tau)+\xi]^2/4\tau\}\,d\xi+\\ &+\frac{1}{2\sqrt{\pi}}\int_0^\tau \frac{J_1[s(\xi)]}{\sqrt{\tau-\xi}}\exp\left\{\frac{-[l(\tau)-l(\xi)]^2}{4(\tau-\xi)}\right\}d\xi-\\ &-\frac{1}{4\sqrt{\pi}}\int_0^\tau f(\xi,0)\frac{[l(\tau)-l(\xi)]}{(\tau-\xi)^{3/2}}\exp\left\{\frac{-[l(\tau)-l(\xi)]^2}{4(\tau-\xi)}\right\}d\xi. \end{aligned} \tag{2.8}$$

Having calculated the third initial moment M_3 of the function f, determining the mass of the particles and connected with supersaturation s by the equation

$$s=q(Q-M_3) \tag{2.9}$$

(q and Q are constants), we obtain the equation

$$\begin{aligned} M_3=&\int_0^\infty fr^3dr=\int_0^\tau J_1(s)\{[l(\tau)-l(\xi)]^3-\\ &-6[l(\tau)-l(\xi)](\xi-\tau)\}\,d\xi+3\int_0^\tau f(\xi,0)\{[l(\tau)-\\ &-l(\xi)]^2-2(\xi-\tau)\}\,d\xi+\int_0^\infty B(r)\{6\tau[l(\tau)-r]+[l(\tau)-r]^3\}\,dr. \end{aligned} \tag{2.10}$$

Thus, the unknown functions $f(\tau,0)$, $M_3(\tau)$, $l(\tau)$ are determined by solving system (2.5), (2.8)-(2.10). After this system is solved, the sought function f is found from Eq. (2.7). If in Eqs. (2.5), (2.8)-(2.10) we pass to the limit with $D_r\to 0$, we obtain the familiar relations in [8].

It is generally very difficult to find an analytical solution for system (2.5), (2.8)-(2.10). Nevertheless, Eq. (1.1) allows a broad set of exact solutions which may prove sufficient to obtain an approximate solution to practical problems.

3. We will seek to solve Eq. (1.1) in the form

$$f = \sum_{i=1}^{\infty} Q_i(\tau) \exp(-\lambda_i r), \quad \lambda_i = \text{const} > 0. \tag{3.1}$$

Inserting Eq. (3.1) into (1.1) and equating to zero the functions dependent on τ with each multiplier $\exp(-\lambda_i r)$, we obtain

$$\frac{dQ_i}{d\tau} - [\lambda_i \varphi(s) + \lambda_i^2] Q_i = 0, \quad i = 1, 2, \ldots \tag{3.2}$$

We calculate the third moment of the function f:

$$M_3 = \sum_{i=1}^{\infty} Q_i(\tau) \int_0^{\infty} r^3 \exp(-\lambda_i r)\, dr = 6 \sum_{i=1}^{\infty} Q_i/\lambda_i^4. \tag{3.3}$$

We take one equation, such as the first, from system (3.2) and write it in the form

$$\frac{\lambda_1}{Q_i}\frac{dQ_i}{d\tau} - \frac{\lambda_i}{Q_1}\frac{dQ_1}{d\tau} = \lambda_1 \lambda_i (\lambda_i - \lambda_1). \tag{3.4}$$

Having integrated system (3.4), we find

$$Q_i^{\lambda_1} = C_i Q_1^{\lambda_i} \exp[\lambda_i \lambda_1 (\lambda_i - \lambda_1)\tau], \tag{3.5}$$

where C_i are constants of integration. Thus, we have determined the relationship between all of the functions Q_i and the single function Q_1. With allowance for (3.5), the expression of (3.3) takes the form

$$M_3 = 6 \sum_{i=1}^{\infty} C_i^{1/\lambda_i} Q_i^{\lambda_i/\lambda_1} \exp[\lambda_i \tau (\lambda_i - \lambda_1)]/\lambda_i^4. \tag{3.6}$$

Inserting (3.6) into (2.9), we determine the relation $s(Q_1)$. Having integrated the first equation of system (3.2), we find

$$\tau = \int \{\lambda_1 \varphi[s(Q_1)] + \lambda_1^2\}^{-1} Q_1^{-1} dQ_1. \tag{3.7}$$

Equations (3.7) and (3.5) determine the sought functions Q_i in an expansion of (3.1).

Solutions of the form (3.1) can be used as test solutions in realizing different numerical and approximate algorithms for solving problems not included in the family (3.1). Also, by using several functions from the set (3.1) and varying the constants λ_i and Q_i, it is possible to approximate initial and boundary conditions and thereby obtain approximate solutions to more complex problems. It should be noted that, besides discrete terms of the form $Q_i(\tau)$ $\exp(-\lambda_i r)$, it is possible to use a continuous distribution of the form $\int_a^b \exp(-\lambda r) Q_\lambda(\tau) d\lambda$. However, if we are concerned with approximating an exact solution, the discrete terms will be quite sufficient in view of the fact that the function B(r) is practically nontrivial only in a finite interval.

Equations (3.2) show that if $Q_i > 0$ at the initial moment of time, then Q_i will subsequently increase, and a steady-state solution to the problem (with $\tau \to \infty$) will be possible if the function $\varphi(s)$ becomes negative, i.e., if in the final stage of the process the crystals grow only as a result of fluctuations in growth rate and dissolve as a result of the convective term in (1.1). The concentration of the carrier phase becomes less than the equilibrium value, i.e., supersaturation will be negative.

The mechanism of the dependence of D_r on the parameters of the process has been studied little. In [6] the coefficient D_r was related to the rate of turbulent mixing in processing units, while in [5] the relation $D_r = D_0 r \varphi(s)$ was used. The latter formula leads to a zero value of the coefficient D_r with zero supersaturation and, thus, in the limit $\tau \to \infty$ no transition to negative supersaturation occurs. A constant value of D_r evidently cannot serve as a good approximation for the entire duration of the process and must be corrected as $s \to 0$.

4. In connection with the foregoing, we will examine the process of mass crystallization, having followed an approach similar to [5] and taken

$$D_r = D_0 r \varphi(s), \quad v(s, r) = (a + br)\varphi(s). \tag{4.1}$$

Here, Eq. (1.1) and auxiliary conditions (1.2)-(1.3) take the following form, with allowance for (2.5)

$$\frac{\partial f}{\partial l} + \frac{\partial}{\partial r}[(a + br) f] = D_0 \frac{\partial}{\partial r}\left(r \frac{\partial f}{\partial r}\right); \qquad (4.2)$$

$$f(0, r) = B(r); \qquad (4.3)$$

$$f|_{r=0} = F(s)/a, \; f|_{r\to\infty} \to 0, \qquad (4.4)$$

where $F(s) = J(s)/\varphi(s)$ is the supersaturation function. Formulation of the complete problem requires determination of the relation $s(l)$, which connects the function F with the variable l. To determine this relation, we change over from Eq. (4.2) to a system of ordinary differential equations

$$dM_0/dl = F[s(M_3)], \; dM_n/dl - nbM_n = n(a + nD_0)M_{n-1}, \qquad (4.5)$$

where $M_n = \int\limits_0^\infty r^n f dr$, $n = 0, 1, 2, 3$. System (4.5) is closed by Eq. (2.9).

With the condition of a linear relation $F(M_3)$, system (4.5) will be linear and easily solvable by standard methods. In practice, the function F can often be linearized in two or three sections and a solution can be obtained for each section. This procedure was followed in [8] with $D_0 = 0$, $b = 0$. As a result of solution of system (4.5), we determine the relation $s(l)$ which, after substitution into boundary condition (4.4), gives the sought relation $F[s(l)]$, and problem (4.2)-(4.4) becomes fully stated.

We make the following substitution in (4.2)-(4.4)

$$h = bl, \; \alpha = a/D_0, \; x = br/D_0, \; g = f \exp h. \qquad (4.6)$$

With allowance for (4.6), problem (4.2)-(4.4) becomes

$$\partial g/\partial h = x\partial^2 g/\partial x^2 + (1 - \alpha - x)\partial g/\partial x; \qquad (4.7)$$

$$g|_{h=0} = B^*(x); \qquad (4.8)$$

$$g|_{x=0} = F(h) \exp h/a, \; g|_{x\to\infty} \to 0. \qquad (4.9)$$

We will seek to solve Eq. (4.7) in the form $g = g_1 + g_2$, where g_1 is a particular solution of Eq. (4.7) satisfying condition (4.8). Noting that Eq. (4.7) has a set of particular solutions of the form

$$L_k^{-\alpha}(x) \exp(-kh), \quad k = 0, 1, 2, \ldots,$$

where $L_k^{-\alpha}$ are Laguerre polynomials, we will seek the function g_1 in the form of a series

$$g_1 = \sum_{k=0}^{\infty} A_k L_k^{-\alpha}(x) \exp(-kh). \qquad (4.10)$$

Having determined the coefficients A_k in (4.10) by expansion of the function $B^*(x)$ into a series in the polynomials $L_k^{-\alpha}$, we obtain

$$g_1 = \sum_{k=0}^{\infty} \frac{k! L_k^{-\alpha}(x) \exp(-kh)}{\Gamma(k - \alpha + 1)} \int\limits_0^\infty \xi^{-\alpha} B^*(\xi) \exp(-\xi) L_k^{-\alpha}(\xi) d\xi, \qquad (4.11)$$

Γ is a gamma function. Having changed the order of integration and summation in (4.11) and using expressions for the generating function of Laguerre polynomials [9], we finally obtain

$$g_1 = \frac{1}{m} \int\limits_0^\infty (\xi\beta)^{-\alpha} B^*(\xi) \exp\left(\frac{x+\xi}{m} - \xi\right) I_{-\alpha}\left(\frac{2\beta}{m}\right) d\xi, \qquad (4.12)$$

$I_{-\alpha}$ is a modified Bessel function, $m = 1 - \exp h$, $\beta = \sqrt{x\xi \exp(-h)}$. Formally obtained solution (4.12) can be substantiated by a method similar to that used in [10], for example. Thus, problem (4.7)-(4.9) reduces to a problem relative to the function g_2 which is homogeneous with respect to the variable h. The boundary condition will be as follows:

$$g_2(h, 0) = F(h) \exp h/a - g_1(h, 0) \equiv F^*(h). \qquad (4.13)$$

We will construct the solution of the above homogeneous problem in the form of the convolution $F^*(h)$ and g_3, where g_3 is the particular solution of Eq. (4.7) with the auxiliary conditions

$$g_3(0, x) = N\delta(x + 0), \; g_3(h, 0) = 0, \qquad (4.14)$$

which describe the process of crystallization without nucleation on N seeds of negligibly small size.

Subjecting Eq. (4.7) to a Laplace transform with respect to the variable h and solving the resulting equation, we find the following expression for the mapping of the function g_3:

$$\overline{g}_3 = N\Gamma(p+\alpha)G(p,\ 1-\alpha,\ x)/\Gamma(1+\alpha), \tag{4.15}$$

where $\overline{g}_3 = \int\limits_0^\infty g_3 \exp(-hp)\,dp$; G is a degenerate hypergeometric function of the second kind. Inverting Eq. (4.15) by means of the Riemann—Mellin formula and using well-known formulas linking degenerate hypergeometric functions and Laguerre polynomials, we obtain

$$g_3 = \frac{N}{\alpha\Gamma(1-\alpha)} \sum_{k=0}^{\infty} (\alpha - k) L_k^{-\alpha}(x) \exp(-kh). \tag{4.16}$$

Series (4.16) can be summed by using the expression for the generating function W of Laguerre polynomials [9]:

$$W(x, y) \equiv (1-y)^{\alpha-1} \exp\left(\frac{xy}{y-1}\right) = \sum_{k=0}^{\infty} L_k^{-\alpha}(x)\, y^k. \tag{4.17}$$

With allowance for (4.17), the final expression for the function g_3 is

$$g_3 = \frac{N}{\alpha\Gamma(1-\alpha)}\left[\alpha W(x, \exp h) + \frac{\partial W(x, \exp h)}{\partial h}\right]. \tag{4.18}$$

Now let us proceed to the construction of the function g_2, which satisfies Eq. (4.7) and homogeneous initial and boundary condition (4.13). As before having subjected Eq. (4.7) and condition (4.13) to the Laplace transform and having solved the resulting equation, we find

$$\overline{g}_2 = \overline{F}^*(p)G(p,\ 1-\alpha,\ x)\Gamma(p+\alpha)/\Gamma(\alpha), \tag{4.19}$$

$\overline{g}_2$ and $\overline{F}^*$ are the mappings of the functions g_2 and F^*, respectively. Representing Eq. (4.19) in the form of the product of two functions $\overline{F}^*(p)$ and $\alpha\overline{g}_3(p)/N$, we obtain an expression for the function g_2 in the form of the convolution

$$g_2 = \frac{\alpha}{N}\int\limits_0^h F^*(h-\xi)\, g_3(\xi, x)\, d\xi. \tag{4.20}$$

Thus, with allowance for Eqs. (4.6), the sum of Eqs. (4.12) and (4.20) is the solution of problem (4.2)-(4.4).

5. We can follow the effect of fluctuations in particle growth rate on the progress of crystallization by comparing the solutions of Eq. (4.2) with $D_0 \neq 0$ and $D_0 = 0$, when the distribution function has the form of a δ-function at the initial moment of time and nucleation is absent. In the case $D_0 \neq 0$, the solution of Eq. (4.2) is Eq. (4.18). In the second case, it is the expression

$$f = bN\delta[a + br - a\exp(bl)], \tag{5.1}$$

which is easily obtained from Eq. (4.2) with $D_0 = 0$ by the method of characteristics, for example, using the homogeneity property of the delta function. Figure 1 qualitatively shows the dynamics over time of the distribution functions for these two cases. Curves 1 and 3 correspond to the function (5.1) at the moments of time t_1 and t_2 ($t_2 > t_1$), while curves 2 and 4 correspond to the function (4.18) for the same moments of time.

In the case $D_0 = 0$ function (5.1) moves along the r axis without distortion at a certain variable rate determined by Eqs. (2.9) and (2.5). A finite value of D_0 leads to "blurring" of the curve of distribution function (4.18). This blurring is also affected by the convective term in (4.2) due to the different rates of growth of crystals of different radii. It should be noted that the latter mechanism was absent when $D_0 = 0$ only because of the selection of the initial distribution in the form of a delta function.

The effect of growth rate fluctuations is also manifest in a certain shift in the maximum of the curve. This effect is manifest in the present nonlinear problem in two ways: both in Eq. (4.2), where D_0 is a parameter, and in Eqs. (4.5), (2.9), and (2.5), where D_0 affects the deformation of time.

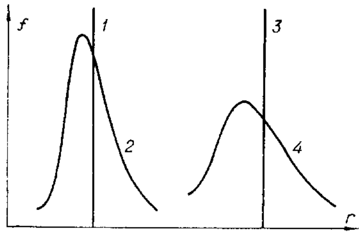

Fig. 1

With an increase in the value of D_0, the degree of blurring of the distribution curves (4.18) increases.

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