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ANALYSIS OF THE DISSOLUTION OF A POLYDISPERSE SYSTEM OF PARTICLES HAVING THE SHAPE OF A PARALLELEPIPED

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A mathematical model based on a crystal size distribution function is proposed for the continuous dissolution of particles having the shape of a parallelepiped. An evolution equation for the undersaturation of the solution is derived. Results of calculations using this equation are presented. A stability analysis of the steady-state solution obtained is carried out.

Introduction. In mathematical description of a number of processes involved in the growth (dissolution) of particles, drops, bubbles, etc., models using particle size distribution functions (PSDF) [1–4] have been widely employed. Such models are sufficiently accurate for practice and are used to determine the size distribution of disperse systems. More detailed and rigorous methods of the mechanics of multiphase systems [5–7] require more complex calculations, and because of inaccuracies and difficulties in closing the basic equations, they offer no advantages over the approach in which PSDF are used.

As a rule, the shape of solid particles in a solution is far from spherical. Nevertheless, the number of papers devoted to investigation of the mass growth of nonspherical inclusions in a carrier medium is very insignificant (see, for example, [8–10]). These papers study the mass growth of a polydisperse system of solid particles in a solution. In addition, of interest is the mass dissolution of particles that have a more complex shape than a sphere and whose geometry is described using several parameters. We are not aware of papers on this topic. In the present study, we analyze the dissolution of a polydisperse system of particles in the shape of a parallelepiped. This particle shape is frequently encountered in nature and engineering and, apparently, it ranks next to a sphere in simplicity.

1. Formulation of the Problem. Let intense mixing occur in the system. In this case, we can assume that the properties of the two-phase system do not depend on spatial coordinates and use the kinetic law of particle dissolution, which is known to hold for large Reynolds numbers [11]. In the kinetic regime, the dissolution of crystal faces does not depend on particle geometry (dimensions) and is only determined by the undersaturation of the solution $C - C^*$ ($C < C^*$). Here C is the concentration of the target component in the solution and C^* is the equilibrium concentration at a specified constant temperature. Thus, we consider isothermal dissolution. The dependence of the rate of change in particle size on the undersaturation is typically linear [11], and in the problem at hand, it has the form

$$\frac{dx}{dt} = U(C - C^*), \qquad \frac{dy}{dt} = V(C - C^*), \qquad \frac{dz}{dt} = W(C - C^*). \tag{1.1}$$

Here t is time, U, V, and W are known positive constants that depend on the hydrodynamic environment in the neighborhood of the particle and physicochemical characteristics (density, viscosity, etc.) of the medium [11]. The shape of the crystal (parallelepiped) is described by three coordinates: length x, width y, and height z. Since the opposite faces of the parallelepiped grow equally, the values of U, V, and W in Eq. (1.1) correspond to the doubled velocity of displacement of the corresponding face.

In formulating the main equations of the problem, we ignore fluctuations in the rate of dissolution of the crystals and the effect of aggregation and cleavage of the crystals on the process considered. For the PSDF $f(x, y, z, t)$, which define the number of particles ΔN in unit volume $\Delta x \Delta y \Delta z$ [i.e., $\Delta N = f(x, y, z, t)\Delta x \Delta y \Delta z$ for small values Δx, Δy, and Δz], the material balance equation for the target solid-phase component is written as

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$$\frac{\partial f}{\partial t} + (C - C^*)U_j \frac{\partial f}{\partial x_j} = \frac{f_*(x_1, x_2, x_3) - f(x_1, x_2, x_3, t)}{\tau}, \tag{1.2}$$

where τ is the mean time of displacement of particles in the system (apparatus in which dissolution is carried out), which is equal to the ratio of the volume of the apparatus to the volumetric consumption of the target component in the crystals, and f_* is the distribution function at the entrance to the system, which, in practice, can contain (describe) undissolved particles that are recycled into the apparatus (fraction of recycle crystals). Generally, f_* can also depend on time. In the present paper, we assume that f_* is a function of only the coordinates x_j ($j = 1, 2, 3$), which describe the crystal shape. For convenience, in some formulas [in particular, (1.2)] we use the notation $x_1 = x$, $x_2 = y$, $x_3 = z$, $U_1 = U$, $U_2 = V$, and $U_3 = W$ and the rule of summation over repeating indices from one to three.

It should be noted that in the particular case of standing systems, where the volumetric expenditure of the solid phase tends to zero, the parameter τ tends to infinity, and the right side of Eq. (1.2) becomes zero (periodic process). Such regimes in the problems of this class were considered in [2, 12, 13].

Equation (1.2) is not sufficient for analysis of the dissolution. We also need to consider the balance of the target substance in the solution, i.e., the evolution equation for the undersaturation

$$\frac{dC}{dt} = \beta(C^* - C)\left(U \int\limits_Q yzf\,dQ + V \int\limits_Q xzf\,dQ + W \int\limits_Q xyf\,dQ\right) - \frac{æC}{\tau}. \tag{1.3}$$

Here the first three (containing integrals) terms on the right side characterize the passage of the substance from the solid phase into the solution (i.e., dissolution itself), and the last term characterizes the exit of the dissolved substance from the system. The term $(C^* - C)U \int\limits_Q yzf\,dQ$ is the product of the area of the face yz, which is perpendicular to the x axis, and the rate of its displacement $U(C^* - C)$, i.e., it designates the increase (decrease) in the volume of a crystal with dimensions x, y, and z in unit time due to change in the coordinate x. After multiplication by $f\,dQ$ and integration, the increments in volume of the entire set of crystals are summed up. The other two integrated terms have the same meaning. All these terms give the increase in volume for the set of crystals due to the growth (dissolutions) of all (three) pairs of faces.

In (1.3) and below, the triple integral over x_j ($j = 1, 2, 3$) in the limits $(0, \infty)$ along each coordinate is denoted by one integral with the symbol Q at the lower limit. In this case, $dQ = dx\,dy\,dz$ is a short form of the product of the differentials. The dissolved substance can move with a rate different from the rate of displacement of the crystals. This is taken into account by the constant æ, which is equal to the ratio of consumption of the target component in the solution to the rate of consumption of the substance in the crystals. In Eq. (1.3), it is assumed that the liquid entering the system has zero concentration of the target component, although for different schemes of the process (for example, in the presence of a recycle) the target component in the solution can penetrate into the system. The parameter β is a shape factor that takes into account the passage of the substance from the crystals into the solution. For a combination of integrals similar to that given in (1.3), we introduce the notation

$$S[f(x, y, z)] = \int\limits_Q (Uyz + Vxz + Wxy) f(x, y, z)\,dQ. \tag{1.4}$$

Although after integration over Q, the operator S does not depend on x, y, and z, we denote the variables and functions by the symbol S, because below we consider cases where the integration variables x, y, are z are combined with some parameters. In this case, the dependence of the operator S on these parameters is of interest.

Equations (1.2) and (1.3) must be supplemented by the initial conditions

$$f\Big|_{t=0} = f_0(x, y, z), \qquad C\Big|_{t=0} = C_0 \quad (C_0 < C^*), \tag{1.5}$$

which describe the size distribution and concentration of the target component at the beginning of the process. As regards boundary conditions, for nonstationary problems of dissolution, they need not be formulated [14] (in contrast to similar problems of mass crystallization from solutions). This is due to the fact that in dissolution problems, the sign of the growth (dissolution) rate is such that the characteristics of Eq. (1.2) arrive at the planes $x = 0$, $y = 0$, $z = 0$ (generally, a particular characteristic comes to one of these planes). Indeed, characteristics (1.2) are solutions of system (1.1), and since $C < C^*$, all coordinates x_j decrease. Therefore, the characteristic lines issue from the region $x > 0$, $y > 0$, $z > 0$, where the initial condition f_0 is specified from physical considerations.

For stationary problems of dissolution, one should employ the condition that the PSDF becomes zero with infinite increase in the crystal dimensions x_j. Actually, the PSDF becomes zero with increase in x_j after intersection of a certain surface in the first quadrant of the coordinate system (x, y, z). This is also valid for the functions f_* and f_0.

The absence of boundary conditions on the planes $x_j = 0$ $(j = 1, 2, 3)$ in dissolution problems introduces considerable changes to analysis compared to problems of mass crystallization, although in the basic equations, only the signs of the rates of change in size alter. In particular, dissolution can give rise to auto-oscillations. In crystallization, auto-oscillations occurs for a rather rapidly increasing function of nucleation rate in the boundary conditions for the equation of the PSDF [15, 16]. We are not aware of proofs of stability or instability for particular dissolution models. [Stability of the steady-state solution of model (1.2), (1.3) is proved below.] In the present paper, the mass dissolution is analyzed on the basis of the PSDF. Different methods of analysis are proposed in e.g., [11, 17]. Because of the absence of boundary conditions on the planes $x_j = 0$ $(j = 1, 2, 3)$, the dissolution problem cannot be analyzed by immediately using the moment approach [1, 18], which is employed in analysis of the kinetic regime of particle growth.

2. Steady-State Solution. In the steady-state regime in Eqs. (1.2) and (1.3), the derivatives with respect to time must be rejected. As an additional condition for the steady-state system (1.2), (1.3), we require that the PSDF tend to zero as $r = (x^2 + y^2 + z^2)^{1/2} \to \infty$. The parameters of the steady-state solution are denoted by the subscript s. The condition $C = C_s$ simplifies integration of Eq. (1.2). The integral of the steady-state equation (1.2) becomes

$$f_s(x, y, z) = \frac{1}{\tau U \Delta C} \int\limits_x^\infty \exp\Big(\frac{x - \eta}{\tau U \Delta C}\Big) f_*\Big(\eta, y + \frac{V}{U}(\eta - x), z + \frac{W}{U}(\eta - x)\Big)\, d\eta$$

$$= \int\limits_0^\infty \exp(-\mu) f_*(x + \mu\tau U \Delta C, y + \mu\tau V \Delta C, z + \mu\tau W \Delta C)\, d\mu. \qquad (2.1)$$

Here $\Delta C = C^* - C_s$.

In (2.1), the unknown quantity ΔC, or more precisely, C_s, is determined using the steady-state equation (1.3), which in view of (2.1) can be written as

$$æC_s = \beta\tau\Delta C \int\limits_0^\infty \exp(-\eta)\, d\eta\, S[f_*(x + \eta\tau U \Delta C, y + \eta\tau V \Delta C, z + \eta\tau W \Delta C)]. \qquad (2.2)$$

Let us show that for physically realizable distributions f_* and realistic parameters of the problem (in particular, the parameters $æ$, β, τ, U, V, and W are positive), Eq. (2.2) has at least one root C_s. The steady-state value of the concentration C_s varies in the interval $C_s \in [0, C^*]$. It should be noted that for $C_s = 0$, the right side of Eq. (2.2) is positive, whereas the left side is equal to zero i.e., the right side is larger than the left side. As $C_s \to C^*$ $(\Delta C \to 0)$, the right side of Eq. (2.2) is equal to $\beta\tau\Delta C S[f_*(x, y, z)]$, i.e., it tends to zero because the factor $\Delta C \to 0$. The left side of (2.2) $æC^* > 0$, i.e., it is larger than the right side. For practically feasible distributions $f_*(x, y, z)$, the right side of (2.2) is a continuous function C_s. Therefore, by virtue of the Bolzano–Cauchy theorem [19, p. 168], Eq. (2.2) is valid at a point $C_s \in (0, C^*)$. This proves the existence of a steady-state regime. For a particular specified function $f_*(x, y, z)$, the root C_s is easily found by modern numerical methods.

Figure 1 shows a graphical method of determining the root C_s. We consider the case where a monodisperse fraction of crystals with dimensions X_*, Y_*, and Z_* is supplied to the entrance to the system, i.e., $f_*(x, y, z) = N_*\delta(x - X_*)\delta(y - Y_*)\delta(z - Z_*)$ [$\delta(z)$ is the Dirac delta function and N_* is the number of crystals supplied at the entrance to the system]. We note that this example is of practical interest. After transformations, Eq. (2.2) reduces to the form

$$G_s = g(G_s) = A\Delta G\Big(B^2(uy_*z_* + vx_*z_* + wx_*y_*)\Big[1 - \exp\Big(-B/\Delta G\Big)\Big]$$

$$- 2B\Delta G(uvz_* + vwx_* + uwy_*)\Big[1 - \Big(1 + B/\Delta G\Big)\exp(-B/\Delta G)\Big]$$

$$+ 6(\Delta G)^2 uvw\Big\{1 - \Big[1 + B/\Delta G + 0.5\Big(B/\Delta G\Big)^2\Big]\exp(-B/\Delta G)\Big\}\Big), \qquad (2.3)$$

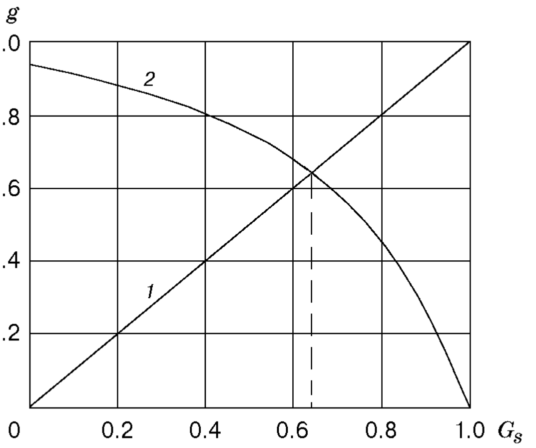

Fig. 1. Plot of the solution of Eq. (2.3) for $\tau = 1$, $u = 1$, $v = 1.2$, $w = 1.5$, $A = 0.45$, and $C^* = 1$: curves 1 and 2 refer to $g = G_s$ and $g(G_s)$, respectively.

where

$$A = \frac{\beta N_*(C^*)^2(\tau U_*)^3}{æ}, \quad B = \frac{1}{\tau C^*}\min\Big(\frac{X_*}{U}, \frac{Y_*}{V}, \frac{Z_*}{W}\Big), \quad G_s = \frac{C_s}{C^*}, \ \Delta G = \frac{\Delta C}{C^*} = 1 - G_s. \tag{2.4}$$

The parameters U, V, W, X_*, Y_*, and Z_* are brought to nondimensional form $u_1 = u = U/U_*$, $u_2 = v = V/U_*$, $u_3 = w = W/U_*$, $x_* = X_*/r_*$, $y_* = Y_*/r_*$, and $z_* = Z_*/r_*$, where the scales of U_* and r_* are the values of U, V, W, X_*, Y_*, and Z_* for which the value of the parameter B in (2.4) is minimal. With this choice of scales, one of the quantities x_*, y_*, and z_*, and, accordingly, one of the quantities u, v, and w are equal to unity. If B takes the indicated minimum value for several values of the ratios X_*/U, Y_*/V, and Z_*/W, we can use any of these equal ratios to determine the scales U_* and r_*. For example, if $X_*/U = Y_*/V < Z_*/W$, we can choose $U_* = U$ and $r_* = X_*$ or $U_* = V$ and $r_* = Y_*$.

To perform calculations, it is important to know which of the crystal dimensions (x, y or z) is the first to disappear during its dissolution, i.e., how the crystal disappears. It is possible that before complete dissolution of crystals having the shape of a parallelepiped, one of the crystal dimensions is much smaller than the remaining. In our case, this is allowed for in the scales of U_* and r_* (among the ratios X_*/U, Y_*/V, Z_*/W, we choose the minimum ratio). Since terms of the form $X_*/(UC^*)$ have the dimension of time, the parameter B in (2.4) represents the nondimensional time during which one of the crystal dimensions becomes zero. For example, if $B = X_*/(UC^*)$, then $U_* = U$ and $r_* = X_*$ and the coordinate x is the first to vanish. If $X_*/U = Y_*/V < Z_*/W$, then the dimensions x and y become zero simultaneously, i.e., at the moment of disappearance, the crystal has an "acicular" shape with nonzero dimension z. In the most "degenerate" case $X_*/U = Y_*/V = Z_*/W$, the three dimensions of the crystal x, y, and z become zero simultaneously with complete dissolution.

The data given in Fig. 1 correspond to the following parameter values: $x_* = 1$, $y_* = 1.5$, $z_* = 1.8$. In this case, $U_* = 1$, $r_* = 1$ and $B = 1$. The curve corresponding to the right side of Eq. (2.3) intersects the vertical axis at $g = 0.936$. The value of the root is $G_s = 0.643$.

3. Proof of the stability of the steady-state solution (2.1). For the mass crystallization process, which is similar to dissolution, stability studies were performed [15, 16, 18, 20]. We are not aware of similar analyses for the mass dissolution process.

In constructing the basic "frequency" equation, we shall follow [20], where we analyzed the effect of the nonisothermal nature of the process on the stability of crystallizer operation. We derive equations for the evolution of a small deviation from the steady-state solution. The unsteady part of the perturbation of the PSDF and undersaturation of the solution is assumed to be an exponential function of time with a complex factor p at the time. This gives an equation whose roots are arranged in the plane $(\mathrm{Re}\,p, \mathrm{Im}\,p)$ so that we can judge the stability of the system (or instability characteristics). We have

$$f(x, y, z, t) = f_s(x, y, z) + \exp(pt)\varphi(x, y, z), \qquad C(t) = C_s + \exp(pt)c. \tag{3.1}$$

It is assumed that $|\varphi| \ll f_s$ and $|c| \ll C_s$. Substituting expressions (3.1) into (1.2) and (1.3) and linearizing in φ and c, we obtain the relations

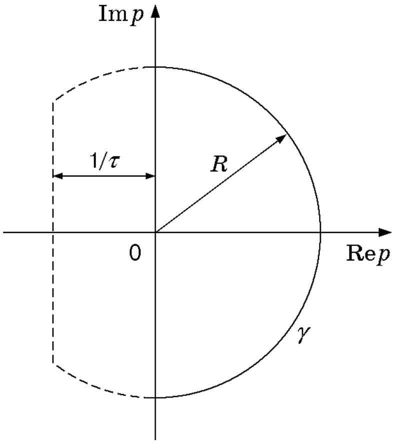

Fig. 2. Contour for determining the number of roots of Eq. (3.4).

$$p\varphi - \Delta C U_j \frac{\partial \varphi}{\partial x_j} + cU_j \frac{\partial f_s}{\partial x_j} + \frac{\varphi}{\tau} = 0, \qquad \Bigl(p + \frac{æ}{\tau}\Bigr)\frac{c}{\beta} - \Delta C S[\varphi(x,y,z)] = cS[f_s(x,y,z)], \tag{3.2}$$

where the operator S is determined in (1.4). Integrating the first equation of (3.2) [which is linear in $\varphi(x,y,z)$] with the proviso that $\varphi \to 0$ as $x,y,z \to \infty$, we obtain

$$\varphi = \frac{c}{\Delta C}\Biggl(f_s(x,y,z) - \int\limits_0^\infty \exp(-\eta) f_s(x + U\chi\eta, y + V\chi\eta, z + W\chi\eta)\, d\eta \Biggr), \tag{3.3}$$

where $\chi = \tau\Delta C/(1 + p\tau)$. Substituting (3.3) into the second equation of (3.2) and performing transformations with allowance for $c \neq 0$, we obtain the following equation for the frequencies of the incipient oscillations:

$$p + \frac{æ}{\tau} + \beta S[f_s(x,y,z)] = -\beta \int\limits_0^\infty \exp\Bigl(-\frac{\eta}{\chi}\Bigr) S\Bigl[U_j \frac{\partial f_s}{\partial x_j}(x + U\eta, y + V\eta, z + W\eta)\Bigr]\, d\eta. \tag{3.4}$$

To make sure that the system is stable, we need to show that Eq. (3.4) has no roots with positive real part. For this, we use the Rushe theorem [21, p. 454]. The expression on the left side of (3.4) has a unique root $p = -æ/\tau - \beta S[f_s(x,y,z)]$, which is in the left half-plane of the plane of the complex variable p, i.e., no roots exist in the right half-plane. Let us show that in the right half-plane, i.e., at Re$\,p \geqslant 0$, the left side of (3.4) surpasses the right side in magnitude. This is needed to construct the contour of γ, which allows us to employ the Rushe theorem. The contour includes a semicircle of radius R drawn from the point $p = 0$ and the vertical line $p = iy$, $y \in (-R, R)$, where i is an imaginary unity (Fig. 2). In fact, we establish the absence of solutions of Eq. (3.4) at Re$\,p > -1/\tau$ $(\tau > 0)$, using the rectilinear boundary of the contour, shifted by $1/\tau$ to the left of the line Re$\,p = 0$, i.e., the boundary of the contour is Re$\,(1/\chi) = 0$ (Fig. 2).

The complex variable p enters into Eq. (3.4) only via the exponent (via the parameter χ) on the right side. It should be noted that with the substitutions of variables necessary for derivation of (3.4), integration over η by rotation of the contour in the case of Re$\,p \geqslant 0$ can always be reduced to the real interval $(0, \infty)$. Let us estimate the right side (3.4) at Re$\,p \geqslant -1/\tau$. We have

$$\Biggl| \int\limits_0^\infty \exp\Bigl(-\frac{\eta}{\chi}\Bigr) S\Bigl[U_j \frac{\partial f_s}{\partial x_j}(x + U\eta, y + V\eta, z + W\eta)\Bigr]\, d\eta \Biggr|$$

$$\leqslant -\int\limits_0^\infty \frac{d}{d\eta} S[f_s(x + U\eta, y + V\eta, z + W\eta)]\, d\eta = S[f_s(x,y,z)]. \tag{3.5}$$

In the derivation of (3.5), we took into account that the derivative of $S[f_s(x + U\eta, y + V\eta, z + W\eta)]$ with respect to η is negative everywhere, which can be seen from the expression

$$\frac{dS}{d\eta}[f_s(x+U\eta, y+V\eta, z+W\eta)] = U_j S\Big[\frac{\partial f_s}{\partial x_j}(x+U\eta, y+V\eta, z+W\eta)\Big]$$

$$= -U^2 \int_0^\infty\int_0^\infty yx f_s(U\eta, y+V\eta, z+W\eta)\, dy\, dz - V^2 \int_0^\infty\int_0^\infty xz f_s(x+U\eta, V\eta, z+W\eta)\, dx\, dz$$

$$- W^2 \int_0^\infty\int_0^\infty xy f_s(x+U\eta, y+V\eta, W\eta)\, dx\, dy - 2\int_Q (UVz + VWx + UWy) f_s(x+U\eta, y+V\eta, z+W\eta)\, dQ < 0.$$

In deriving this expression, we took into account the conditions $U > 0$, $V > 0$, $W > 0$, and $f_s > 0$, the shape of the domain of integration, and dependence (1.4).

From (3.5) it follows that the right side of Eq. (3.4) is not larger than the third term of $\beta S[f_s(x,y,z)]$ on the left side (which is real). (From physical considerations, the parameters æ, β, τ, U, V and W are positive.) Inequality (3.5) is also satisfied for $\mathrm{Re}\, p \geqslant 0$. In this region,

$$\Big| p + \frac{æ}{\tau} + \beta S[f_s(x,y,z)]\Big| > \Big|\beta \int_0^\infty \exp\Big(-\frac{\eta}{\chi}\Big) S\Big[U_j \frac{\partial f_s}{\partial x_j}(x+U\eta, y+V\eta, z+W\eta)\Big]\, d\eta\Big|. \tag{3.6}$$

We assume that the function f_* is such (for example, continuous) that substitution of f_s from (2.1) into (3.4) ensures that the right side of (3.4) in χ is analytic at $\mathrm{Re}\, p \geqslant 0$. Since the right and left sides (3.4) are analytic inside the contour γ and are continuous on it and inequality (3.6) is satisfied, the Rushe theorem is applicable [21]. From this theorem it follows that inside the contour bounded by the line γ and the line segment $\mathrm{Re}\, p = 0$, which makes the contour closed, the left side of (3.4) $p + æ/\tau + \beta S[f_s(x,y,z)] = 0$ and the complete equation (3.4) have identical number of roots. However, for any parameter values, the equation $p + æ/\tau + \beta S[f_s(x,y,z)] = 0$ has no roots inside this contour. Hence, neither Eq. (3.4) has roots here. As $R \to \infty$, Eq. (3.4) has no roots in the right half-plane $\mathrm{Re}\, p > 0$, i.e., the steady-state solution (2.1) is stable against small perturbations. Using inequality (3.5), it is possible to show that the real part of the roots of (3.4) is not larger than $-1/\tau$, i.e., there is a particular stability margin.

4. Unsteady Regime. With the stability of the steady-state solution, the unsteady regime describes the transition to the steady-state regime. To solve problem (1.2)–(1.5), it is reasonable to introduce variables related to the characteristics of Eq. (1.2):

$$\frac{d\lambda_x}{dt} = U(C^* - C), \quad \frac{d\lambda_y}{dt} = V(C^* - C), \quad \frac{d\lambda_z}{dt} = W(C^* - C), \quad \lambda_x(0) = \lambda_y(0) = \lambda_z(0) = 0. \tag{4.1}$$

Formulas (4.1) differ from the equations of characteristics (1.1) for (1.2) only in sign [14] but (4.1) also specifies initial conditions for the functions λ_x, λ_y, and λ_z. Along the characteristic, Eq. (1.2) can be written as

$$\frac{df}{dt} = \frac{f_*(x(t), y(t), z(t)) - f(x(t), y(t), z(t), t)}{\tau}.$$

The formal solution [$C(t)$, and, hence, $\lambda_j(t)$ are considered known functions of time] has the form

$$f(x,y,z,t) = \exp\Big(-\frac{t}{\tau}\Big)\Big(f_0(x+\lambda_x(t), y+\lambda_y(t), z+\lambda_z(t))$$
$$+ \frac{1}{\tau}\int_0^t \exp\Big(\frac{\eta}{\tau}\Big) f_*(x+\lambda_x(t)-\lambda_x(\eta), y+\lambda_y(t)-\lambda_y(\eta), z+\lambda_z(t)-\lambda_z(\eta))\, d\eta\Big). \tag{4.2}$$

The function f in (4.2) satisfies Eq. (1.2) and the initial condition (1.5), which is easily verified by immediate calculation, using the definition of the functions λ_x, λ_y, and λ_z according to (4.1). Calculating the integrals over Q in Eq. (1.3), we obtain

$$\frac{dC}{dt} = \beta(C^* - C)\exp\Big(-\frac{t}{\tau}\Big)\bigg(S[f_0(x+\lambda_x(t), y+\lambda_y(t), z+\lambda_z(t))]$$
$$+ \frac{1}{\tau}\int_0^t \exp\Big(\frac{\eta}{\tau}\Big) S[f_*(x+\lambda_x(t)-\lambda_x(\eta), y+\lambda_y(t)-\lambda_y(\eta), z+\lambda_z(t)-\lambda_z(\eta))]\, d\eta\bigg) - æ\frac{C}{\tau}, \tag{4.3}$$

$$C(0) = C_0.$$

Equations (4.3) and (4.1) form a closed system of equations for the concentration $C(t)$ and the auxiliary functions $\lambda_x(t)$, $\lambda_y(t)$, and $\lambda_z(t)$. Having solved problem (4.1), (4.3), we can consider the function f in (4.2) determined because the functions $\lambda_j(t)$ $(j = 1, 2, 3)$ needed to calculated it are obtained.

As an example, we solve this problem for the case where a monodisperse fraction of crystals with dimensions X_*, Y_*, and Z_* is supplied at the entrance to the system, i.e., $f_*(x, y, z) = N_*\delta(x-X_*)\delta(y-Y_*)\delta(z-Z_*)$. The initial function $f_0(x, y, z)$ is taken equal to zero. The integral of the Dirac delta functions in (4.3) is easy to calculate. As a result, we obtain a special case of Eq. (4.3) in nondimensional form:

$$\frac{dG}{d\zeta} = æ\Bigg[A(1-G)\exp(-\zeta)\int\limits_0^{\zeta}\exp(\mu)\,d\mu\Big(u[\hat{y}+\omega_y(\mu)-\omega_y(\zeta)][\hat{z}+\omega_z(\mu)-\omega_z(\zeta)]$$

$$+\,v[\hat{x}+\omega_x(\mu)-\omega_x(\zeta)][\hat{z}+\omega_z(\mu)-\omega_z(\zeta)]$$

$$+\,w[\hat{x}+\omega_x(\mu)-\omega_x(\zeta)][\hat{y}+\omega_y(\mu)-\omega_y(\zeta)]\Big)\prod_{j=1}^{3}H(\hat{x}_j+\omega_j(\mu)-\omega_j(\zeta))-G\Bigg],\quad G\Big|_{\zeta=0}=G_0=\frac{C_0}{C^*};\qquad(4.4)$$

$$\frac{d\omega_j}{d\zeta} = u_j(1-G),\qquad \omega_j\Big|_{\zeta=0}=0\quad(j=1,2,3).\qquad(4.5)$$

Here the parameters u_j are defined in the formulation of Eqs. (2.3) and (2.4); $H(z)$ is the Heaviside function $[H(z) = 1$ at $z \geqslant 0$, $H(z) = 0$ at $z < 0]$, $\zeta = t/\tau$ is nondimensional time, $G = C/C^*$ is the nondimensional concentration, $\omega_j(\zeta) = \lambda_j(t)/(\tau U_* C^*)$ are nondimensional functions of $\lambda_j(t)$ $(j = 1, 2, 3)$, and the parameter A is defined by to (2.4); $\hat{x}_j = X_{*j}/(\tau U_* C^*)$.

The occurrence of Heaviside functions in (4.4) is due to the change of nature of the solution at the moment when a particular fraction of crystals of the system completely dissolved (disappeared), i.e., when the first crystals with dimensions X_*, Y_*, and Z_* injected into the apparatus completely dissolved. In this case, integration in (4.4) is performed from a value $\mu = \mu_*(\zeta)$ (and not from zero) until a particular moment is reached. We note that the case in point is a particular choice of the functions f_* and f_0. Generally, in the presence of very small crystals in the system, disappearance of particles can begin immediately after they were placed in the apparatus.

The linear dependence of the dissolution rates (1.1) on the undersaturation simplifies the problem. In this case, two integrals of system (4.5) can be obtained. Nondimensionalization of the parameters according to (2.3) and (2.4) implies that a pair of the values U_j and X_{*j} $(j = 1, 2, 3)$ for which the value of the parameter B in (2.4) is minimal makes the corresponding nondimensional quantities equal to unity. For definiteness, we assume that $u = 1$ and $x_* = 1$, i.e., $U_* = U$ and $r_* = X_*$ (see Fig. 1). Then, it is reasonable to express the functions $\omega_y(\zeta)$ and $\omega_z(\zeta)$ in (4.5) in terms of $\omega_x(\zeta)$. We obtain

$$\omega_y(\zeta) = v\omega(\zeta),\qquad \omega_z(\zeta) = w\omega(\zeta),\qquad \omega(\zeta) = \omega_x(\zeta),\qquad(4.6)$$

where the coefficient of the function $\omega_x(\zeta)$ is dropped for brevity. We note that relations (4.6) are valid only in the general case with satisfaction of (1.1) and not only for the conditions considered. With the use of (4.6), problem (4.4), (4.5) reduces to the system

$$\frac{dG}{d\zeta} = æ\Bigg[A(1-G)\exp(-\zeta)\int\limits_0^{\zeta}\exp(\mu)\,d\mu\Big(u[\hat{y}+v(\omega(\mu)-\omega(\zeta))][\hat{z}+w(\omega(\mu)-\omega(\zeta))]$$

$$+\,v[B+\omega(\mu)-\omega(\zeta)][\hat{z}+w(\omega(\mu)-\omega(\zeta))]$$

$$+\,w[B+\omega(\mu)-\omega(\zeta)][\hat{y}+v(\omega(\mu)-\omega(\zeta))]\Big)H(B+\omega(\mu)-\omega(\zeta))-G\Bigg],\quad G(0)=G_0;\qquad(4.7)$$

$$\frac{d\omega}{d\zeta} = 1-G,\qquad \omega(0)=0,\qquad(4.8)$$

where $B = \hat{x}$. In addition, of the three Heaviside functions in (4.4) that “cut off” integration, we retain only the function that defines the lower limit of integration over μ.

Generally, problem (4.7), (4.8) is solved numerically. For analytical solution of this problem, it is possible to employ the iteration method. In this case, the function ω is easily determined from (4.8): $\omega(\zeta) = \Delta G\zeta$. Substitution of this expression into (4.7) (into the integral term) leads to a sufficiently complex equation (which is typical of the iteration method) for $\zeta < \xi = B/\Delta G$ [see (2.4)] and a simple equation for $\zeta > \xi$:

$$\frac{dG}{d\zeta} = æ(G_s - G) \qquad (\zeta > \xi). \tag{4.9}$$

From calculation results it follows that if Eq. (4.9) is used over the entire range of time, for the initial conditions (4.7) its solutions

$$G(\zeta) = G_s + (G_0 - G_s)\exp(-æ\zeta) \tag{4.10}$$

is closer to the exact solution than the solution obtained by the iteration method, which at $\zeta < \xi$, instead of (4.9) uses a different equation following from (4.7) and equalities $\omega(\zeta) = \Delta G\zeta$. This is due to the fact that as a first approximation of the iteration method, we used a steady-state solution that is more realistic for rather large times. As a result, approximation (4.9) for the complete equation (4.7) in the region $\zeta < \xi$ can be exacter than the approximation of the iterative method in this interval.

Thus expression (4.10) can be used as an approximation of the exact solution and next it can be employed for approximate representation of the function $\omega(\zeta)$, using solution (4.8), in the form

$$\omega(\zeta) = (1 - G_s)\zeta - (G_0 - G_s)[1 - \exp(-æ\zeta)]/æ. \tag{4.11}$$

This, in turn, allows us to obtain an approximate expression for the PSDF. Apparently, formula (4.11) can also be used for approximate determination of the PSDF (4.2) [taking into account the dependence between λ_j and ω_j and relation (4.6)] in the general problem of mass dissolution. In the nondimensional variables, this solution has the form

$$f(x,y,z,t) = \exp(-\zeta)\Big(f_0(\hat{x} + u\omega(\zeta), \hat{y} + v\omega(\zeta), \hat{z} + w\omega(\zeta))$$

$$+ \int\limits_0^{\zeta} \exp(\mu) f_*(\hat{x} + u[\omega(\zeta) - \omega(\mu)], \hat{y} + v[\omega(\zeta) - \omega(\mu)], \hat{z} + w[\omega(\zeta) - \omega(\mu)])\, d\mu\Big), \tag{4.12}$$

where for symmetry, we introduce the factor u, which, by virtue of (4.6) is equal to unity. Thus, an approximate solution of problem (1.2)–(1.5) is given by formulas (4.10)–(4.12) with allowance for (4.6). In this case, to determine the approximate solution, one need to find the steady-state concentration G_s from equation (2.2). However, it should be noted that for small times, the solution is affected by the function f_0, which was ignored in the derivation of (4.11).

The calculation results are presented in Fig. 3. It is evident that the approximate values of $G(\zeta)$ are in good agreement with numerical results. The approximate dependence $\omega(\zeta)$ is not sown in Fig. 3 because for the given parameters and scales of variables, the numerical and approximate (4.11) solutions practically coincide.

In the construction of the numerical algorithm, the integral term in (4.7) was approximated by the trapezoid rule, and the derivatives in (4.7) and (4.8) were approximated by the first-order finite differences of $dG/d\zeta = [G(\zeta + h) - G(\zeta)]/h$ and $d\omega/d\zeta = [\omega(\zeta + h) - \omega(\zeta)]/h$, where $h > 0$ is the step of the difference scheme. It should be noted that the dependence $\omega(\zeta)$ is rather close to a straight line practically throughout the interval.

5. Rate of Disappearance of Particles. For the mass crystallization process, the most important characteristic is the rate of nucleation of the new phase, and for dissolution, this is the rate of disappearance of particles. Let us formulate the equation of change in the number of crystals N, determined by the quantity $\int\limits_Q f(x,y,z)\, dQ$. For this, we integrate Eq. (1.2) over Q. As a result, we obtain

$$\frac{dN}{dt} = -I + \frac{N_* - N}{\tau}, \tag{5.1}$$

where $N_* = \int\limits_Q f_*(x,y,z)\, dQ$ is the number of crystals entering the system. The rate of disappearance of particles I in (5.1) is defined by the relation

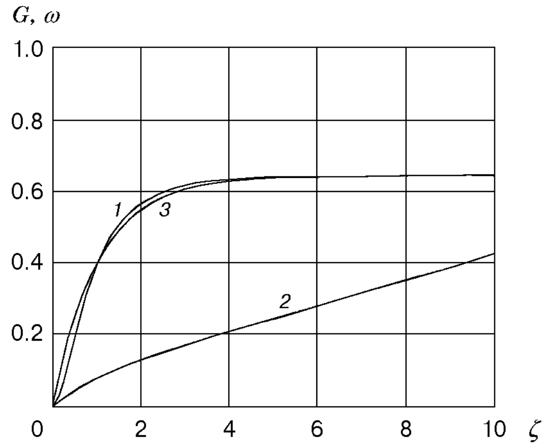

Fig. 3. Dependences $G(\zeta)$ and $\omega(\zeta)$ for the unsteady solution of Eqs. (4.7), (4.8) for $G_0 = 0$, $æ = 0.95$, $U_* = 1$, $\tau = 1$, $x_* = 1$, $y_* = 1.5$, $z_* = 1.8$, $u = 1$, $v = 1.2$, $w = 1.5$, $A = 0.45$, $C^* = 1$: curves 1 and 3 refer to $G(\zeta)$ [1 is the numerical solution and 3 is the calculation using formula (4.10)] and curve 2 refers to $0.1\omega(\zeta)$.

$$I = (C^* - C)\left(U\int_0^\infty\int_0^\infty f(0,y,z,t)\,dy\,dz + V\int_0^\infty\int_0^\infty f(x,0,z,t)\,dx\,dz + W\int_0^\infty\int_0^\infty f(x,y,0,t)\,dx\,dy\right). \tag{5.2}$$

For the periodic process (in the basic equations $\tau \to \infty$) according to (5.1), this quantity characterizes the rate of change in the number of particles dN/dt in the system. In this case, (periodic process) we do not consider the inflow of particles into the system with rate N_*/τ and their outflow with rate N/τ, unlike in the general case. In this connection, we can consider the efficiency of the dissolution process in this system (apparatus). This quantity (rate coefficient ν) means the ratio of the rate of disappearance of crystals in the steady-state process to the rate of their penetration into the system, i.e., according to (2.1),

$$\nu = \frac{\tau I_s}{N_*} = 1 - \frac{N_s}{N_*} = \frac{1}{N_*}\int_0^\infty \exp\Big(-\frac{\eta}{\tau\Delta C}\Big)\,d\eta\left(U\int_0^\infty\int_0^\infty f_*(\eta U, y+\eta V, z+\eta W)\,dy\,dz\right.$$

$$\left. + V\int_0^\infty\int_0^\infty f_*(x+\eta U, \eta V, z+\eta W)\,dx\,dz + W\int_0^\infty\int_0^\infty f_*(x+\eta U, y+\eta V, \eta W)\,dx\,dy\right). \tag{5.3}$$

For the case considered in the present paper, i.e., inflow of a monodisperse fraction of crystals with dimensions X_*, Y_*, and Z_*, the function $f_*(x,y,z) = N_*\delta(x - X_*)\delta(y - Y_*)\delta(z - Z_*)$. In this case, from formula (5.3) it follows that

$$\nu = \exp\,(-B/\Delta G). \tag{5.4}$$

For the parameters corresponding to the example in Fig. 1, we have $\nu \approx 0.061$.

The parameter ν is introduced to determine the fraction of crystals that disappeared.

Expression (5.3) can be simplified. For example, if $\tau U_*\Delta C \ll 1$, the function f_* in (5.3) can be expanded in a Taylor series in powers of η in the neighborhood of the point (x,y,z). Restricting ourselves to the first two terms of this expansion, we obtain the approximate equality

$$\nu \simeq \frac{\tau\Delta C}{N_*}\left(U\int_0^\infty\int_0^\infty f_*(0,y,z)\,dy\,dz + V\int_0^\infty\int_0^\infty f_*(x,0,z)\,dx\,dz + W\int_0^\infty\int_0^\infty f_*(x,y,0)\,dx\,dy\right). \tag{5.5}$$

Formulas (5.3)–(5.5) express the numerical efficiency of dissolution because they determine the fraction of dissolved particles. We can also introduce the mass (or volumetric) efficiency. For the steady-state process, we define it as the ratio of the volume of particles that passed into the solution $M(f_*) - M(f_s)$ to the volume of particles that entered the system $M(f_*)$:

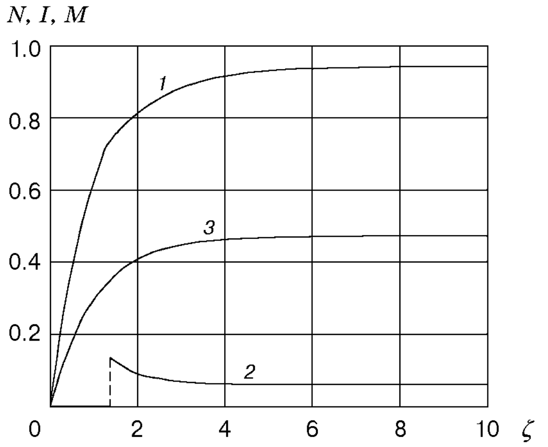

Fig. 4. Results of unsteady solution of equations (4.7) and (4.8): curve 1 refers to the number of particles $N(\zeta)$, curve 2 refers to the rate of disappearance of particles $I(\zeta)$, and curve 3 refers to the total volume of particles $M(\zeta)$.

$$\sigma = 1 - M(f_s)/M(f_*).$$

Here $M(f) = \int\limits_Q xyzf(x,y,z)\,dQ$ is the moment characteristic of the PSDF, which depends on the mean volume of the crystals. Multiplying the steady-state equation (1.2) by xyz and integrating over these variables (over Q) in the limits $(0,\infty)$, we obtain

$$\tau\Delta C \int\limits_Q (Uyz + Vxz + Wxy) f_s(x,y,z)\,dQ = M(f_*) - M(f_s).$$

From this, using the steady-state equation (1.3), we obtain the volumetric rate of dissolution

$$\sigma = \frac{\tau\Delta C}{M(f_*)} \int\limits_Q (Uyz + Vxz + Wxy) f_s(x,y,z)\,dQ = \frac{æ C_s}{\beta M(f_*)}.$$

In the case of the monodisperse function f_* (see Fig. 1), we have $\sigma = G_s = 0.643$. For $\tau U\Delta C \ll 1$, we obtain a formula similar to (5.5)

$$\sigma \simeq \frac{\tau\Delta C}{M(f_*)}\biggl[S[f_*(x,y,z)] - \tau\Delta C\biggl(U^2 \int\limits_0^\infty\int\limits_0^\infty yzf_*(0,y,z)\,dy\,dz + V^2 \int\limits_0^\infty\int\limits_0^\infty xzf_*(x,0,z)\,dx\,dz$$

$$+ W^2 \int\limits_0^\infty\int\limits_0^\infty xyf_*(x,y,0)\,dx\,dy + 2\int\limits_Q (UVz + VWx + UWy) f_*(x,y,z)\,dQ\biggr)\biggr],$$

which contains the characteristics of the function f_* at the entrance.

The time dependence of the rate of disappearance of crystals constructed using relation (5.2) is shown in Fig. 4 (curve 2). As might be expected, disappearance of particles begins some time ($\zeta \simeq 1.35$) after the beginning of the process. This time corresponds to the complete dissolution of the first crystals that entered the system. In addition, Fig. 4 shows time dependences of the number of particles N (curve 1) and the total volume of particles M (curve 3). For $\zeta \simeq 1.35$, curve 1 has inflection (discontinuity of the derivative). As $\zeta \to \infty$, the dependences take values that correspond to the steady-state solution ($N_s \simeq 0.94$, $I_s \simeq 0.06$, and $M_s \simeq 0.47$), which can also be obtained using (2.1).

Conclusions. The mass dissolution problem (1.2)–(1.5) reduces to system (4.7), (4.8) by using equalities (4.6), which, in turn, follow from the laws of dissolution (1.1). We note that the theory described is easily extended to a more general case than the law of decrease in crystal dimensions considered in this paper. Some manipulations and results of this work are valid if the parameters U, V, and W in (1.1) are considered nonlinear functions $C - C^*$ that vanish for $C = C^*$. If these functions are different, relations (4.6) are not valid.

The proportional growth of crystal faces (4.6) allows one to describe the dissolution of crystals in the shape of a parallelepiped by the one-parameter model applicable for the mass dissolution of spherical particles. Problem (1.2)–(1.5) includes this version as a particular case. The function f is written as $f = F(x, y, z, t)\delta(yU - xV)\delta(zU - xW)$. With substitution of this dependence into (1.2), the terms containing derivatives of the δ-functions are reduced, and the regular part of the function f satisfies the equation

$$\frac{\partial \psi}{\partial t} + U(C - C^*)\frac{\partial \psi}{\partial x} = \frac{\psi_*(x) - \psi(x,t)}{\tau}, \qquad \psi(x,t) = F\Big(x, x\,\frac{V}{U}, x\,\frac{W}{U}, t\Big),$$

where the function $\psi_*(x) = F_*(x, x\,V/U, x\,W/U)$ is related to the function f_*. The second equation of the dissolution model (1.3) can be written as

$$\frac{dC}{dt} = \frac{\beta(C^* - C)VW}{U^3}\int\limits_0^\infty x^2\psi(x,t)\,dx - \frac{æC}{\tau}.$$

These equations with the modified initial condition (1.5) for ψ form a model for the dissolution of spherical particles and describe the dissolution of particles whose dimensions satisfy the ratios $x : y : z = U : V : W$, i.e., from one of the quantities x, y, and z, it is easy to determine the remaining. This follows from the initial structure of the function f and relations (4.6).

System (1.2), (1.3) leads to the law of conservation of material during dissolution. To derive it, we need to multiply (1.2) by xyz and integrate it over Q. Taking into account (1.3), we obtain the equation

$$\frac{d}{dt}\Big(C + \beta M(f)\Big) = \frac{\beta(M(f_*) - M(f)) - æC}{\tau},$$

which, in particular, leads to the dependence between steady-state values of C_s and $M(f_s)$.

In the particular case $f_* \equiv 0$, problem (4.1), (4.3) can be reduced to the system of ordinary differential equations if analytical integration of f_0 over Q in (4.3) is possible.

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