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DESCRIPTION OF MASS GROWTH OF CRYSTALS FROM SOLUTIONS WITH ALLOWANCE FOR THE DISAPPEARANCE OF CRYSTAL FACES DURING CRYSTAL GROWTH

A. I. Moshinskii

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Mass crystallization was studied on the basis of a crystal-size distribution function for a kinetic law of growth of faces (when the growth rate of a crystal face does not depend on the size and shape of the face) and with allowance for vanishing of individual faces during crystal growth. It is proposed that the crystallization problem should be reduced to a system of equations that admit analytical solutions in some cases of practical interest.

An approach involving the introduction of a particle-size distribution function [1–6] is often used in describing the behavior of polydisperse particle systems in the presence of a phase transition [the growth of fog drops in condensation, the reverse process of vanishing of drops due to evaporation, crystallization and dissolution of solid particles in a solution in the presence of supersaturation (undersaturation), etc.]. Knowledge of this function allows one to determine the variation in time of all quantities of applied interest: the number of particles, their average size and specific surface, the total volume of all particles of the solid phase, etc. As a rule, a certain effective size of crystals (for example, the volume average radius for crystals of complex shape) is taken as the size (radius). This simplifies the calculations markedly and applies to liquid polydisperse systems. However, there are some disadvantages in this representation of the geometry of a solid particle. Thus, for example, experimental observations of the course of mass crystallization showed a series of attendant phenomena that complicate the description of crystal growth. For example, crystal growth is often accompanied by fluctuations of the crystal-growth rate [5–7]. Crystals stick together, break up, and, what is especially important for the subject of the present work, different crystal faces grow at different characteristic rates, etc. [6, 7]. The latter, as is known [8, 9], leads not only to a change in the crystal shape with time but also to the disappearance of some crystal faces. It is clear that the conventional approach does not permit keeping track of the change in the crystal shape and the experimentally observed disappearance of some crystal faces. Usually, portions of crystals produced in experiments show a certain spread of crystal sizes and geometry. This certainly adversely affects the accuracy of prediction of the main characteristics of the process. Naturally, in connection with the aforesaid, research faces the problem of extending the conventional approaches (one-parameter in size) to the geometry of crystals growing in a supersaturated solution.

The problem of the mass growth of crystals is originally formulated as a nonlinear problem since the rate of their growth (dissolution) of crystals depends on the characteristics of the sought quantity — the size-distribution function. Therefore, analytical solutions of the corresponding problems are obtained rather rarely, and any change in the formulation of the problem can complicate it appreciably. Approaches to the solution of such problems are described in [3–7, 10, 11].

A natural step in the development of the description of mass crystallization involves the use of several parameters to determine the shape of a crystal. This increases the dimensionality of the equations and, hence, complicates analysis of them [12–15]. Therefore, there has not been considerable progress in this line

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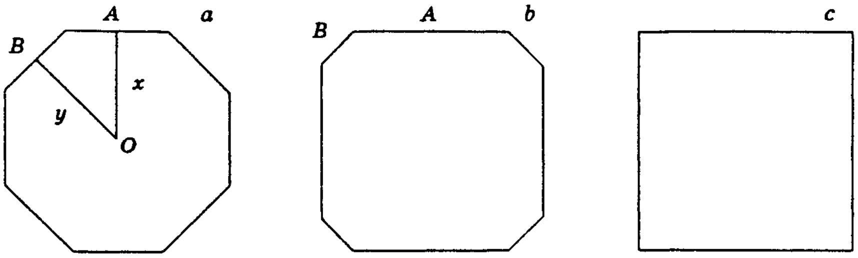

Fig. 1

of research. In addition, we are not aware of mathematical simulations of the mass growth of crystals in a solution that take into account the known phenomenon [8, 9] of the disappearance of crystal faces during growth. In this connection, the main goal of the present paper is to discuss and develop an approach to the description of mass crystallization in the presence of the indicated effect.

1. Formulation of the Equations of the Problem. As a first step in this direction, we consider the crystallization process without additional complications. We assume that crystal faces grow in a kinetic regime, i.e., the growth rate of a particle does not depend on the particle size (it depends only on the supersaturation of the solution C). In the definition of supersaturation, we assume that the equilibrium concentration C_* at a given constant temperature is subtracted from the concentration of the dissolved solid phase. This difference is the supersaturation of the solution. Therefore, complete elimination of supersaturation corresponds to $C = 0$. Fluctuations of the growth rate of crystals are not taken into consideration.

It is easy to see that, depending on the shape of the crystal, the characteristics of the crystal (volume, surface area, etc.) are frequently written in a specific form. Therefore, to illustrate the general approach without going into unimportant details, we consider a particular crystal (one-parameter family), whose cross section is a $2k$-gon with equal and parallel opposite sides (Fig. 1a shows a crystal of an octagonal cross section). In this case, there are two different sets of faces, and faces of the same set are not adjacent to one another, i.e., each vertex of the polygon in the cross section is formed by faces of different sets. Representatives of each set are denoted in Fig. 1a. These are faces A and B with different growth rates (x and y are the distances from the center O of the crystal to faces A and B, respectively). Figure 1b shows the crystal before the disappearance of face B (and related faces). A particular case where some faces disappear is a regular k-gon (Fig. 1c) in the cross section. In addition, all crystals have the shape of a prism of height z.

It is easy to see that the volume of the crystal can be expressed in terms of x and y. After simple calculations, we have

$$Q = kz\frac{2xy - (x^2 + y^2)\cos\varphi}{\sin\varphi}, \qquad \cos\varphi \leqslant \frac{x}{y} \leqslant \frac{1}{\cos\varphi}, \qquad \varphi = \frac{\pi}{k}. \tag{1.1}$$

We assume that the integer k is larger than two to eliminate the case where the crystal has the shape of a rectangle and hence vanishing of faces does not occur. The cases where the ratio of the parameters x and y reaches the limiting values $1/\cos\varphi$ and $\cos\varphi$ correspond to the degeneration of the $2k$-gon to a regular k-gon. The motion of faces A and B and the bases of the prism in the kinetic regime is defined by the formulas

$$\frac{dx}{dt} = U(C), \qquad \frac{dy}{dt} = V(C), \qquad \frac{dz}{dt} = W(C), \tag{1.2}$$

where $U(C)$, $V(C)$, and $W(C)$ are known functions of supersaturation only, which are usually nearly proportional: $U(C) \approx UC$, $V(C) \approx VC$, and $W(C) \approx WC$ for $U = \text{const}$, $V = \text{const}$, and $W = \text{const}$. After vanishing of some faces, the remaining faces begin to grow. We assume that opposite faces (Fig. 1) grow by the same law and the function $W(C)$ describes the variation in the height of the prism, i.e., the actual growth rate of the corresponding faces is half W. The variables x, y, and z determine all the geometric characteristics (in particular, the dimensions in different directions) of the crystal. We shall call them size parameters.

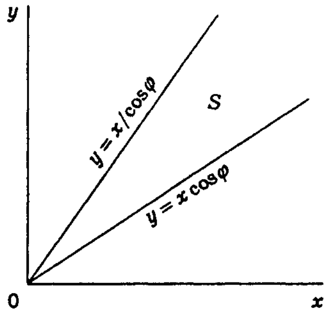

Fig. 2

The condition $\cos\varphi \leqslant x/y \leqslant 1/\cos\varphi$ for the absence of degeneration of the $2k$-gon restricts the range of crystal parameters x and y in which all the $2k$ crystal faces grow to the interior angle (Fig. 2) in the plane of parameters x and y. In the region S bounded by the rays $y = x\cos\varphi$ and $y = x/\cos\varphi$ and the plane $z = 0$, the evolution of the crystal-size distribution function f obeys the equation

$$\frac{\partial f}{\partial t} + U(C)\frac{\partial f}{\partial x} + V(C)\frac{\partial f}{\partial y} + W(C)\frac{\partial f}{\partial z} = 0, \tag{1.3}$$

i.e., the function f varies only as a result of crystal growth. Here t is the time, and the physical meaning of the function f is that this function, being multiplied by the element of the "volume" $dxdydz$, gives the number of crystals whose size parameters are in the ranges $(x, x+dx)$, $(y, y+dy)$, and $(z, z+dz)$ for small values of dx, dy, and dz.

If, during growth, the crystal "falls" on the plane $y = x\cos\varphi$ or $y = x/\cos\varphi$, the mechanism of growth of crystals changes because k faces disappear. For the crystal geometry considered here, it is easy to see [8, 9], that the most rapidly growing faces of the crystal disappear first of all. In this case, it is expedient to describe separately particular fractions of crystals (the cross-sectional shapes of a regular k-gon) on these planes. The corresponding distribution functions will be designated as f_+ and f_-. The evolution of these functions is affected not only by the crystal growth at rates $U(C)$ or $V(C)$ in the plane (x,y) at a rate $W(C)$ along the z axis but also by the inflow (outflow) of crystals to (from) the region S between the planes $y = x(\cos\varphi)^{\pm 1}$. To determine these flows, it is useful to derive an equation that describes the number of crystals $N_S = \int\limits_S f(x,y,z,t)\,dx\,dy\,dz$ in the region S. We integrate Eq. (1.3) over the region S. After some calculations we have

$$\frac{dN_S}{dt} = (V - U\cos\varphi)\int\limits_0^\infty\int\limits_0^\infty f(x, x\cos\varphi, z, t)\,dx\,dz$$

$$+ (U - V\cos\varphi)\int\limits_0^\infty\int\limits_0^\infty f(y\cos\varphi, y, z, t)\,dy\,dz + J_S(C). \tag{1.4}$$

Here the last term on the right side is due to nucleation. We shall discuss it later, but for now note that the expression $(V - U\cos\varphi)f(x, x\cos\varphi, z, t)\,dx\,dz$ gives the density of the inflow (outflow) of crystals in the region S through the plane $y = x\cos\varphi$. Similarly, the expression $(U - V\cos\varphi)f(y\cos\varphi, y, z, t)\,dy\,dz$ describes the inflow (outflow) of crystals to (from) the region S through the plane $y = x/\cos\varphi$. The terms inflow and outflow are used for the corresponding signs of the combinations of the growth rates $(V - U\cos\varphi)$ and $(U - V\cos\varphi)$, which can also be negative. We now write equations for the distribution functions f_+ and f_-:

$$\frac{\partial f_+}{\partial t} + V(C)\frac{\partial f_+}{\partial y} + W(C)\frac{\partial f_+}{\partial z} = (U(C) - V(C)/\cos\varphi)f(y/\cos\varphi, y, z, t); \tag{1.5}$$

$$\frac{\partial f_-}{\partial t} + U(C)\,\frac{\partial f_-}{\partial x} + W(C)\,\frac{\partial f_-}{\partial z} = (V(C) - U(C)/\cos\varphi) f(x, x/\cos\varphi, z, t). \tag{1.6}$$

The physical meaning of the functions f_+ and f_- is that they, being multiplied by the element $dy\,dz$ and $dx\,dz$, give the number of crystals whose size parameters are in the ranges $(y, y+dy)$ and $(z, z+dz)$ for f_+ or $(x, x+dx)$ and $(z, z+dz)$ for f_- for small values of dy, dz and dx, dz.

We derive an equation that defines the evolution of supersaturation. This equation represents the balance of material with passage from the solution to the solid phase (crystals). In this case, it is necessary to take into account the contribution of the three functions f, f_+, and f_- to the balance. For the functions f_+ and f_- the inflow into the solid phase is described by formulas that are identical with accuracy up to notation. In constructing necessary relations we use the general expression for the rate of volume change of the material that passed to the solid phase: $\int\limits_Q f(dQ/dt)\,dq$. Here integration is extended to the entire range of crystal size parameters, and Q is defined by formula (1.1). Then, it is necessary to express dQ/dt in terms of the growth rates of faces. Having performed the indicated operation with the functions f, f_+, and f_-, we arrive at the equation

$$\frac{dC}{dt} = -\beta\Big\{ \int\limits_S f(x,y,z,t)\,dx\,dy\,dz \{2z[(x - y\cos\varphi)V(C) + (y - x\cos\varphi)U(C)]$$

$$+[2xy - (x^2 + y^2)\cos\varphi]W(C)\}/\sin\varphi + \tan\varphi\Big[2U(C)\int\limits_0^\infty\int\limits_0^\infty xzf_-(x,z,t)\,dx\,dz$$

$$+W(C)\int\limits_0^\infty\int\limits_0^\infty x^2 f_-(x,z,t)\,dx\,dz + 2V(C)\int\limits_0^\infty\int\limits_0^\infty yzf_+(y,z,t)\,dy\,dz$$

$$+W(C)\int\limits_0^\infty\int\limits_0^\infty y^2 f_+(y,z,t)\,dy\,dz\Big]\Big\}. \tag{1.7}$$

The coefficient β characterizes the relation of the shape, the density, and other characteristics of the crystal to the geometric parameters. It serves primarily to establish a valid relation between the characteristics of the target component in the solution (the function C) and in the solid phase (the functions f, f_+, and f_-) for passage of the material from the solution into crystals. The analytical form of β depends on the definition (normalization) of the distribution function and concentration. If, following [14] we assume that the product $C\Omega$ (Ω is the total volume occupied by the solution) gives the total mass of the dissolved material, then for our definition of the distribution functions, we have $\beta = \rho k/\Omega$, where ρ is the density of the solid phase.

2. Additional Conditions. To complete the formulation of the crystallization problem, it is necessary to formulate the initial and boundary conditions for system (1.3) and (1.5)–(1.7). The initial conditions describe the state of the system at the time $t = 0$ and are generally of the form

$$f\Big|_{t=0} = f_0(x,y,z), \quad C\Big|_{t=0} = C_0, \quad f_+\Big|_{t=0} = f_0^+(y,z), \quad f_-\Big|_{t=0} = f_0^-(x,z). \tag{2.1}$$

The boundary conditions for Eqs. (1.5) and (1.6) relate the distribution function on the natural boundary of the range of crystal size parameters with the rate of formation of new crystals. In [12, 13], the conventional boundary condition of nucleation was extended to the case of dependence of the crystal volume on three parameters for the kinetic and diffusion laws of growth of particles in the shape of a parallelepiped. The conditions included the Dirac delta function $\delta(X)$. This means that the neighborhood of the coordinate origin was of significance to the formulation of the boundary condition related to the rate of nucleation. Following [12, 13], we represent the boundary conditions for Eqs. (1.5) and (1.6), which are non-one-dimensional in the coordinates related to the crystal sizes, in the form

$$V(C)f_+\Big|_{y=0} = J_{y+}(C)\delta(z), \qquad W(C)f_+\Big|_{z=0} = J_{z+}(C)\delta(y),$$
$$U(C)f_-\Big|_{x=0} = J_{x-}(C)\delta(z), \qquad W(C)f_-\Big|_{z=0} = J_{z-}(C)\delta(x), \tag{2.2}$$

where the rates of formation of a new phase J_{x-}, J_{y+}, J_{z+}, and J_{z-} depend only on the supersaturation of the solution. Generally speaking, nuclei of the new phase have nonzero dimensions in contrast to (2.2). However, in mass crystallization, the typical dimensions of crystals are such that one can ignore with high accuracy the dimensions of a nucleus, setting them equal to zero. This is usually done in problems of mass crystallization of salts from solutions [7, 10–14, etc.], whereas in related problems (see, for example, [4]), it may be important to take into account the size of a nucleus of a new phase.

The definition of functions of the type J_{x-}, J_{y+}, J_{z+}, and J_{z-} is an independent problem, which is not considered here. We note, however, that the corresponding equations for J_{x-}, J_{y+}, J_{z+}, J_{z-}, etc., are similar only in form to the equations of mass crystallization, whereas they contain much smaller characteristic particle sizes. Furthermore, when fluctuations of the growth rate of crystals are taken into account, the boundary conditions should be supplemented by the requirement of a rather fast decrease in the distribution function with an infinite increase in the crystal size parameters x, y, and z.

For Eq. (1.3), the boundary condition related to the rate of nucleation is more specific. Since it is adopted that nuclei of the new phase have zero dimensions, this condition is related to the behavior of the function f in a neighborhood of the trihedral angle formed by the planes $y = x(\cos\varphi)^{\pm 1}$ and $z = 0$ with vertex at the point $x = 0$, $y = 0$, $z = 0$. The difference from the previous variant is also determined by the dimensionality of the problem in space coordinates. In the interior of the acute angle for $z = \text{const}$ (Fig. 2), the problem can be reduced to the problem in the first quadrant for the auxiliary variables ξ and η. In this case, the calculations can be performed in the new variables where appropriate. In particular, it is expedient to convert from the trihedral angle formed by three mutually perpendicular planes, as in [12, 13], to the trihedral angle formed by the planes $y = x(\cos\varphi)^{\pm 1}$ and $z = 0$ ($x > 0$, $y > 0$, and $z > 0$). The necessary formulas of transformation of the variables x and y have the form

$$\xi = \frac{x - y\cos\varphi}{\sin\varphi}, \qquad \eta = \frac{y - x\cos\varphi}{\sin\varphi}, \qquad x = \frac{\xi + \eta\cos\varphi}{\sin\varphi}, \qquad y = \frac{\xi\cos\varphi + \eta}{\sin\varphi}. \tag{2.3}$$

The Jacobian of the transformation (2.3), which should be used in calculation of the double integral in (1.7), is equal to unity: $\partial(x,y)/\partial(\xi,\eta) = 1$. After transformation to the variables ξ and η, both the integrand in the triple integral (1.7) and the region of integration become simpler. The equation for the distribution function (1.3) is written in the new coordinates as

$$\frac{\partial f}{\partial t} + V_\xi(C)\frac{\partial f}{\partial \xi} + V_\eta(C)\frac{\partial f}{\partial \eta} + W(C)\frac{\partial f}{\partial z} = 0. \tag{2.4}$$

Here $V_\xi(C) = [U(C) - V(C)\cos\varphi]/\sin\varphi$ and $V_\eta(C) = [V(C) - U(C)\cos\varphi]/\sin\varphi$. Thus, it is obvious that the equation retained its form with definite (effective) growth rates along the axes ξ and η. It is important to note that, in contrast to Eq. (1.3), where U and V are considered positive in crystallization, the effective rates $V_\xi(C)$ and $V_\eta(C)$ can also be negative. This can be called fictitious dissolution along a corresponding coordinate.

If $V_\xi > 0$ and $V_\eta > 0$, the boundary conditions for Eq. (2.4), according to [12, 13], take the form

$$V_\xi(C)f\Big|_{\xi=0} = J_\xi(C)\delta(\eta)\delta(z), \quad V_\eta(C)f\Big|_{\eta=0} = J_\eta(C)\delta(\xi)\delta(z),$$
$$W(C)f\Big|_{z=0} = J_z(C)\delta(\xi)\delta(\eta), \tag{2.5}$$

where $J_\xi(C)$, $J_\eta(C)$, and $J_z(C)$ are three "components" of nucleation [12, 13]. The calculation formulas contain their sum: $J_S(C) = J_\xi(C) + J_\eta(C) + J_z(C)$. Note that, like (2.5), the boundary conditions in [12, 13] lead to consistent results with an appropriate choice of coefficients of the equation. The fact is that, assuming zero

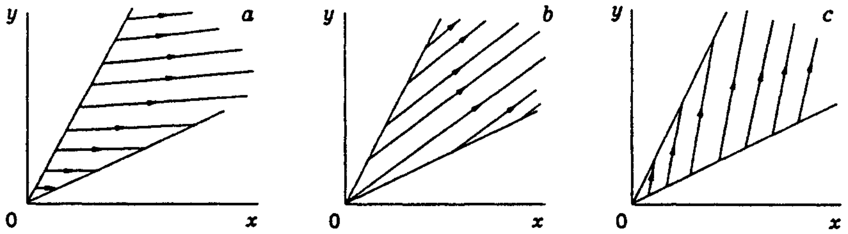

Fig. 3

dimensions of nuclei of the new phase, we allow the crystal to take any permissible shape (in agreement with the crystal lattice) literally at once, by joining the first molecules of the dissolved material. This shape is determined by the laws of growth of the size parameters x, y, and z.

The boundary conditions contain the δ function, i.e., they have a singular character. In principle, in the planes $\xi = 0$ and $\eta = 0$ [which correspond, according to (2.3), to $y = x/\cos\varphi$ and $y = x\cos\varphi$] some other conditions (outside of the neighborhood of the coordinate origin) can also be imposed. However, by virtue of the possibility of negative coefficients at the derivatives $\partial f/\partial\xi$ and $\partial f/\partial\eta$ in (2.4), these conditions should be formulated with allowance for this circumstance, or, more precisely, the structure of the field of characteristics for Eq. (2.4) and the intersections of lines on which the boundary conditions [16] are specified. Note that integrating Eq. (2.4) over the quadrant $0 < \xi < \infty$ and $0 < \eta < \infty$ with allowance for (2.3) and (2.5) and the above remark on the boundary conditions, we obtain formula (1.4) for the number of particles in the region S. It is easy to show that the variation in time of the total number of crystals described by the functions f, f_+, and f_-, is defined by the equation

$$\frac{dN}{dt} = \frac{dN_S}{dt} + \frac{dN_+}{dt} + \frac{dN_-}{dt} = J_S(C) + J_+(C) + J_-(C), \tag{2.6}$$

where N_S, N_+, and N_- are the total numbers of crystals described by the functions f, f_+, and f_-, respectively (the integrals of these functions over crystal size parameters in the entire region of their definition); $J_+ = J_{y+} + J_{z+}$, $J_- = J_{x-} + J_{z-}$, and $N = N_S + N_+ + N_-$ is the total number of particles in all states.

3. Variants of Formulation of the Problem. Momental Equations. Before proceeding to solution of Eqs. (1.3) and (1.5)–(1.7) subject to conditions of the form (2.1), (2.2), and (2.5), we discuss possible versions of formulation of the problem in relation to the kinetics of crystal growth. Integration of Eq. (1.3) in the region S depends largely on the field of its characteristics. In this case, besides two degenerate cases, there are three typical variants. Equations (1.2) define the fields of characteristics for Eq. (1.3). It is easy to see that the crystal growth in the z direction (the face z cannot disappear) influences the disappearance of crystal faces in an indirect manner (via supersaturation, which is common for the entire mass of crystals). Therefore, the "main events" proceed in the same manner for all z (or t) in the plane (x, y). As a result, the formulation of the problem for Eq. (1.3) depends on the field of characteristics in the plane (x, y). For the slope of the characteristics for $z = \text{const}$ in the plane (x, y), from (1.2) we have $dy/dx = V(C)/U(C)$.

The three cases of formulation of the crystallization problem are characterized by the inequalities $V/U < \cos\varphi$, $\cos\varphi < V/U < 1/\cos\varphi$, and $V/U > 1/\cos\varphi$ [Fig. 3, where face A tends to disappear during crystal growth (a), the faces do not disappear during crystal growth (b), and face B tends to disappear during crystal growth (c)]. From Fig. 3 it is evident that, in the first and third cases, the same characteristic intersects both boundaries of the region: $y = x(\cos\varphi)^{\pm 1}$. This means that the boundary condition can be set only on one of the boundaries (on the other boundary, the solution of the problem is calculated). In direct problems of the development of the process with time, boundary conditions should be specified on the curve $y = x/\cos\varphi$ in the first variant and on the curve $y = x\cos\varphi$ in the third variant. The transfer of the solution along the characteristics with time is shown in Fig. 3 by arrows.

In the second case, boundary conditions should be imposed on both curves $y = x(\cos\varphi)^{\pm 1}$. Note that in the second case, disappearance of crystal faces does not occur. It is evident from Fig. 3 that disappearance occurs on that curve $y = x(\cos\varphi)^{\pm 1}$ at which the characteristics of Eq. (1.3) appear. The degenerate variants mentioned above are cases where the characteristic lines are parallel to the rays $y = x/\cos\varphi$ and $y = x\cos\varphi$, i.e., the equalities $U(C) = V(C)\cos\varphi$ or $U(C)\cos\varphi = V(C)$ hold. Note that since the field of characteristics depends just on the function C and via it on time, it is in principle possible that the pattern of the field of characteristics changes from one variant (Fig. 3) to the other with time.

A popular approach to the solution of crystallization problems is the momental approach, which is unfortunately not always applicable. It can be used when a closed system of momental equations is obtained without any approximate methods. In a one-parameter description of the crystal size by the radius of a sphere whose volume is equal to the volume of the crystal when the crystal-growth rate bears a power-law relation to this radius, $V \cong r^{-\alpha}$ and $\alpha = \text{const}$ (a rather general case that includes a number of widely used growth regimes), as is shown in [17], the momental approach is applicable to discrete values of the parameter $\alpha = 3/n - 1$, where n is an integer, in particular, for $\alpha = 0$ (the kinetic regime, as in the present paper). Note that in some cases one should introduce moments of fractional order. The momental approach is also suitable for some other (not power) laws of crystal growth, for example, the equation $V \cong a_0 + a_1 r$ (a_0 and a_1 are constants). The variants listed above refer to a description of crystal growth that is "one-parameter in size." For crystals in the form of a parallelepiped, the possibility of using the momental approach is shown in [12].

We introduce the following notation for the moments of the functions f, f_+, and f_-:

$$M_{i,j,k} = \int\limits_0^\infty \int\limits_0^\infty \int\limits_0^\infty \xi^i \eta^j z^k f(\xi/\sin\varphi + \eta\cot\varphi, \xi\cot\varphi + \eta/\sin\varphi, z, t)\, d\xi\, d\eta\, dz,$$

$$M_{i,j}^{+} = \int\limits_0^\infty \int\limits_0^\infty y^i z^j f_+(y, z, t)\, dy\, dz, \quad M_{i,j}^{-} = \int\limits_0^\infty \int\limits_0^\infty x^i z^j f_-(x, z, t)\, dx\, dz \quad (i,\ j,\ k = 0,\ 1,\ 2\ldots). \tag{3.1}$$

We obtain equations for the moments (3.1) by multiplying the equations for the functions f, f_+, and f_- by $\xi^i\eta^j z^k$, $y^i z^j$, and $x^i z^j$, respectively, and integrating from zero to infinity over all the coordinates that describe the particle sizes. As a result, we have

$$\frac{dM_{i,j,k}}{dt} = iV_\xi(C)M_{i-1,j,k} + jV_\eta(C)M_{i,j-1,k} + kW(C)M_{i,j,k-1} \quad (i,\ j,\ k \geqslant 1); \tag{3.2}$$

$$\frac{dM_{i,j}^{+}}{dt} = iV(C)M_{i-1,j}^{+} + jW(C)M_{i,j-1}^{+} - V_\eta(C)\sin\varphi(\cos\varphi)^i \nu_{ij} \quad (i,\ j \geqslant 1); \tag{3.3}$$

$$\frac{dM_{i,j}^{-}}{dt} = iU(C)M_{i-1,j}^{-} + jW(C)M_{i,j-1}^{-} - V_\xi(C)\sin\varphi(\cos\varphi)^i \mu_{ij} \quad (i,\ j \geqslant 1), \tag{3.4}$$

where

$$\nu_{ij} = \int\limits_0^\infty \int\limits_0^\infty y^i z^j f(y, y\cos\varphi, z, t)\, dy\, dz, \qquad \mu_{ij} = \int\limits_0^\infty \int\limits_0^\infty x^i z^j f(x\cos\varphi, x, z, t)\, dx\, dz.$$

These equations are derived under the assumption that i, j, and k are larger than unity. When one (or two) of the subscripts are equal to zero, relations (3.2)–(3.4) are somewhat changed:

$$\frac{dM_{0,j,k}}{dt} = jV_\eta(C)M_{0,j-1,k} + kW(C)M_{0,j,k-1} + V_\xi(C)(\sin\varphi)^{j+1}\mu_{jk} \quad (j,\ k \geqslant 1); \tag{3.5}$$

$$\frac{dM_{i,0,k}}{dt} = iV_\xi(C)M_{i-1,0,k} + kW(C)M_{i,0,k-1} + V_\eta(C)(\sin\varphi)^{i+1}\nu_{ik} \quad (i,\ k \geqslant 1),$$

$$\frac{dM_{i,j,0}}{dt} = iV_\xi(C)M_{i-1,j,0} + jV_\eta(C)M_{i,j-1,0} \quad (i,\ j \geqslant 1),$$

$$\frac{dM_{0,0,k}}{dt} = J_S(C)\delta_{0,k} + V_\xi(C)\sin\varphi\mu_{0k} + V_\eta(C)\sin\varphi\nu_{0k} \quad (k \geqslant 0), \tag{3.6}$$

$$\frac{dM_{i,0,0}}{dt} = iV_\xi(C)M_{i-1,0,0} + V_\eta(C)(\sin\varphi)^{i+1}\nu_{i0} \quad (i \geqslant 1),$$

$$\frac{dM_{0,j,0}}{dt} = jV_\eta(C)M_{0,j-1,0} + V_\xi(C)(\sin\varphi)^{j+1}\mu_{j0} \quad (j \geqslant 1);$$

$$\frac{dM^+_{0,j}}{dt} = jW(C)M^+_{0,j-1} - V_\eta(C)\sin\varphi\nu_{0j} \quad (j \geqslant 1),$$
$$\frac{dM^+_{i,0}}{dt} = iV(C)M^+_{i-1,0} - V_\eta(C)\sin\varphi(\cos\varphi)^i\nu_{i0} \quad (i \geqslant 1), \quad \frac{dM^+_{0,0}}{dt} = J_+(C) - V_\eta(C)\sin\varphi\nu_{00}; \tag{3.7}$$

$$\frac{dM^-_{0,j}}{dt} = jW(C)M^-_{0,j-1} - V_\xi(C)\sin\varphi\mu_{0j} \quad (j \geqslant 1),$$
$$\frac{dM^-_{i,0}}{dt} = iU(C)M^-_{i-1,0} - V_\xi(C)\sin\varphi(\cos\varphi)^i\mu_{i0} \quad (i \geqslant 1), \quad \frac{dM^-_{0,0}}{dt} = J_-(C) - V_\xi(C)\sin\varphi\mu_{00}. \tag{3.8}$$

Here $\delta_{0,k}$ is the Kronecker delta. The equation for $M_{0,0,0}$ is actually already derived [see (1.4)] because $N_S = M_{0,0,0}$. By virtue of the equalities $N_+ = M^+_{0,0}$ and $N_- = M^-_{0,0}$, it is easy to see that the addition of Eqs. (1.4), (3.7), and (3.8) leads to Eq. (2.6). Using (2.3) and the definition of the momental functions (3.1), we write Eq. (1.7) as

$$\frac{dC}{dt} = -\beta[2V(C)M_{1,0,1} + 2U(C)M_{0,1,1} + 2W(C)M_{1,1,0}/\sin\varphi + \cot\varphi W(C)(M_{2,0,0} + M_{0,2,0})$$
$$+ \tan\varphi[2U(C)M^-_{1,1} + 2V(C)M^+_{1,1} + W(C)(M^-_{2,0} + M^+_{2,0})]]. \tag{3.9}$$

Combining (3.9) with Eqs. (3.5), (3.6) multiplied by the corresponding factors for the given values of the parameters i, j, and k and integrating, we obtain

$$C + \beta[2M_{1,1,1} + \cot\varphi(M_{2,0,1} + M_{0,2,1}) + \tan\varphi(M^-_{2,1} + M^+_{2,1})] = \text{const}, \tag{3.10}$$

where the constant on the right side is determined by the initial conditions (2.1), which allow initial data for the momental equations to be obtained. Relation (3.10) is the law of conservation of mass in crystallization.

4. Examples. As noted above, the solution of the problem depends on the structure of the field of characteristics of the basic equation for the distribution function (1.3) or (2.4). The case where $\cos\varphi < V/U < 1/\cos\varphi$ (it is called the second case) is simplest for analysis. In this case, the basic (complete) system of equations of the problem are Eqs. (1.4) ($N_S = M_{0,0,0}$) and (3.3)–(3.9) for values of subscripts that give derivatives of the sought functions on the left side: C, $M_{0,0,0}$, $M_{0,0,1}$, $M_{0,1,0}$, $M_{1,0,0}$, $M_{1,0,1}$, $M_{0,1,1}$, $M_{1,1,0}$, $M_{2,0,0}$, $M_{0,2,0}$, $M^-_{0,0}$, $M^-_{0,1}$, $M^-_{1,0}$, $M^-_{1,1}$, $M^-_{2,0}$, $M^+_{0,0}$, $M^+_{0,1}$, $M^+_{1,0}$, $M^+_{1,1}$, and $M^+_{2,0}$. All the terms containing integrals of the function f [i.e., ν_{ij} and μ_{ij} for values of the subscripts i and j that correspond to Eqs. (3.3)–(3.8)] should be considered known (specified).

Thus, we have a closed system of 20 ordinary differential equations subject to the initial conditions obtained from (2.1) after calculation of the corresponding moments. This system of equations involves no serious difficulties for numerical methods, although use of just one parameter as a characteristic of the crystal size (an equivalent radius) led to a system of only four differential equations for the kinetic regime of crystal growth. For the practically significant functions $U(C)$, $V(C)$, $W(C)$, $J_S(C)$, $J_+(C)$, and $J_-(C)$, an analytical solution can also be obtained (see similar cases in [17]).

To obtain an approximate analytical solution, it is possible to use the method proposed in [18]. After the function $C(t)$ is found, it is not hard to obtain the distribution functions f, f_+, and f_- from the linear equations (1.3) [or (2.4)], (1.5), and (1.6), containing the already known coefficients, under appropriate additional conditions with known coefficients.

Variants that are more complicated for solution (the first variant $V/U < \cos\varphi$ and the third variant $V/U > 1/\cos\varphi$) are considered similarly, because they coincide with accuracy to notation. Therefore, we restrict ourselves to only the third variant and, for brevity, use some additional conditions in simplified form. The characteristic features of the equations will be retained in this case. In the third variant, one cannot use the procedure of the second variant, because the terms in the form of integrals of the type ν_{ij} and μ_{ij} for definite values of the subscripts are unknown (in the second variant, they are known). Arbitrary definition of these terms will generally lead to contradiction in attempts to find the function f on one of the curves $y = x(\cos\varphi)^{\pm 1}$ using Eqs. (1.3). Therefore, we shall proceed as follows. We shall temporarily regard C as a known function of time. Hence, we obtain a number of relations, which will be further correlated with one another. As a result, we arrive at the desired system of crystallization equations for $V/U > 1/\cos\varphi$. We first consider Eq. (1.3) subject to the additional conditions

$$f\Big|_{t=0} = f_0(x,y,z), \qquad f\Big|_{y=x\cos\varphi} = 0, \qquad J_S(C) = 0, \tag{4.1}$$

where the last relation (the absence of nucleation for the crystals described by the function f) is supplemented by the appropriate conditions (2.5) for $J_\xi = J_\eta = J_z = 0$. In addition, we assume that $f_+\big|_{t=0} = 0$ and $J_+(C) = 0$. These conditions and (2.5) allow us to obtain a zero solution for the function f_+ $[f_+(y,z,t) = 0]$. The solution of Eq. (1.3) subject to conditions (4.1) has the form

$$f(x,y,z,t) = f_0[x - \lambda_x(t), y - \lambda_y(t), z - \lambda_z(t)]H[x - \lambda_x(t)]H[y - \lambda_y(t)]H[z - \lambda_z(t)],$$
$$H(z) = \begin{cases} 1, & z \geqslant 0, \\ 0, & z < 0, \end{cases} \tag{4.2}$$

as is easily verified by direct check. Here $(x,y,z) \in S$, $H(z)$ is the Heaviside function, and the functions λ_x, λ_y, and λ_z, which define the characteristic of Eq. (1.3) that issues from the coordinate origin, satisfy the relations

$$\frac{d\lambda_x}{dt} = U(C), \quad \frac{d\lambda_y}{dt} = V(C), \quad \frac{d\lambda_z}{dt} = W(C), \quad \lambda_x\Big|_{t=0} = \lambda_y\Big|_{t=0} = \lambda_z\Big|_{t=0} = 0. \tag{4.3}$$

The additional conditions for Eq. (1.6) are taken in full form from (2.1) and (2.2). With allowance for (4.2), Eq. (1.6) takes the form

$$\frac{\partial f_-}{\partial t} + U(C)\frac{\partial f_-}{\partial x} + W(C)\frac{\partial f_-}{\partial z} = -\tan\varphi V(C) f_0[x - \lambda_x(t), x/\cos\varphi$$
$$- \lambda_y(t), z - \lambda_z(t)]H[x - \lambda_x(t)]H[x/\cos\varphi - \lambda_y(t)]H[z - \lambda_z(t)]. \tag{4.4}$$

A solution of (4.4) can be obtained using a Laplace transform over the variables x and z. After some manipulations for the function f_-, we obtain

$$f_-(x,z,t) = f_0^-[x - \lambda_x(t), z - \lambda_z(t)]H[x - \lambda_x(t)]H[z - \lambda_z(t)]$$
$$+ \int_0^t J_-[C(\zeta)]\delta[x - \lambda_x(t) + \lambda_x(\zeta)]\delta[z - \lambda_z(t) + \lambda_z(\zeta)]\, d\zeta$$
$$- \tan\varphi \int_0^t V_\xi[C(\zeta)]d\zeta f_0\{x - \lambda_x(t), [x + \lambda_x(\zeta) - \lambda_x(t)]/\cos\varphi$$
$$- \lambda_y(\zeta), z - \lambda_z(t)\}H[x - \lambda_x(t)]H\{[x + \lambda_x(\zeta) - \lambda_x(t)]/\cos\varphi - \lambda_y(\zeta)\}H[z - \lambda_z(t)]. \tag{4.5}$$

We calculate moments of the function f_- that are necessary for Eq. (1.7) or (3.9):

$$M_{i,j}^- = \int_0^\infty\int_0^\infty [x + \lambda_x(t)]^i[z + \lambda_z(t)]^j f_0^-(x,z)\, dx\, dz + \int_0^t J_-[C(\zeta)][\lambda_x(t) - \lambda_x(\zeta)]^i[\lambda_z(t) - \lambda_z(\zeta)]^j\, d\zeta$$
$$- \tan\varphi \int_0^t V_\xi[C(\zeta)]\, d\zeta \int_0^\infty\int_0^\infty [x + \lambda_x(t) + \cos\varphi\lambda_y(\zeta) - \lambda_x(\zeta)]^i$$
$$\times [z + \lambda_z(t)]^j f_0[x + \cos\varphi\lambda_y(\zeta) - \lambda_x(\zeta), x/\cos\varphi, z]\, dx\, dz. \tag{4.6}$$

In the derivation of (4.6), we used the inequality $\lambda_y > \lambda_x/\cos\varphi$, which follows from (4.3), and the inequality $V(C) > U(C)/\cos\varphi$ (the third case). For the necessary concrete values of i and j (we need the moments $M^-_{1,1}$ and $M^-_{2,0}$), formulas (4.6) become somewhat simpler. The formula for the moments of the function f $M_{1,0,1}$, $M_{0,1,1}$, $M_{1,1,0}$, $M_{2,0,0}$, and $M_{0,2,0}$, which are necessary for Eq. (3.9), are expressed by simple quadratures, but, in the general case, the functional dependence of the corresponding moments on the variables λ_x, λ_y, and λ_z can be rather complicated. For brevity, we give only the formula for $M_{1,0,1}$:

$$M_{1,0,1} = \int_0^\infty\int_0^\infty\int_0^\infty \xi z f_0[\xi/\sin\varphi + \eta\cot\varphi - \lambda_x(t), \xi\cot\varphi + \eta/\sin\varphi - \lambda_y(t), z - \lambda_z(t)]$$
$$\times H\,[\xi/\sin\varphi + \eta\cot\varphi - \lambda_x(t)]H[\xi\cot\varphi + \eta/\sin\varphi - \lambda_y(t)]H[z - \lambda_z(t)]\,d\xi\,d\eta\,dz. \tag{4.7}$$

It can be somewhat rearranged by refining the region of integration that follows from the properties of the Heaviside function.

With allowance for (4.6), (4.7), etc., and the equalities $M^+_{1,1} \equiv M^+_{2,0} \equiv 0$, relations (3.9) and (4.3) form a closed system of equations. Solving this system, i.e., finding the functions $C(t)$, $\lambda_x(t)$, $\lambda_y(t)$, and $\lambda_z(t)$, we obtain a solution of the crystallization problem because the distribution functions f and f_- will be expressed explicitly in terms of the functions $C(t)$, $\lambda_x(t)$, $\lambda_y(t)$, and $\lambda_z(t)$. Note that this system can be decreased in order if we first seek a solution in the form $C = C(\lambda_x)$, $\lambda_y = \lambda_y(\lambda_x)$, and $\lambda_z = \lambda_z(\lambda_x)$ and then relate the parameter λ_x with time using the quadrature

$$t = \int_0^{\lambda_x} U^{-1}[C(\zeta)]\,d\zeta.$$

A further solution in this case can be performed for concrete functions $f_0(x, y, z)$ and $J_-(C)$. For illustration, we restrict ourselves to one example, using the following expressions for the necessary functions: $f_0(x, y, z) = N_S\delta(x - x_0)\delta(y - y_0)\delta(z - z_0)$, $J_-(C) \equiv 0$, and $f_0^-(x, z) = N_-\delta(x - x_0^-)\delta(zz_0^-)$. Here x_0, y_0, z_0, x_0^-, and z_0^- are certain constants. Any distribution function of a similar (δ-shaped) form will be called a monodisperse function. The functions $U(C)$, $V(C)$, and $W(C)$ are assumed to be linear: $U(C) = UC$, $V(C) = VC$, and $W(C) = WC$ at U, V, and $W =$ const. It should be noted that this is of great practical significance because theoretical considerations and experimental data show that the growth rate is proportional (or nearly proportional) to C. This allows one to use a relation of the type $V = AC$ for each crystal face and (if necessary) to calculate the correction by the perturbation method [19]. The functional relations of the growth rate of crystals with supersaturation and the differences of them from the law $V = AC$ ($A =$ const) are discussed using experimental facts, for example, in [8, 20].

Calculation of integral (4.6) leads to the expression

$$M^-_{i,j} = N_-[x_0^- + \lambda_x(t)]^i[z_0^- + \lambda_z(t)]^j + N_S[x_0 + \lambda_x(t)]^i[z_0 + \lambda_z(t)]^j H\Big[\lambda_x(t)\Big(\frac{V}{U} - \frac{1}{\cos\varphi}\Big) - \xi_0\Big], \tag{4.8}$$

where $\xi_0 = x_0/\sin\varphi - y_0\cot\varphi$ [see (2.3)]. In deriving (4.8), we used the equality

$$\frac{\lambda_x(t)}{U} = \frac{\lambda_y(t)}{V} = \frac{\lambda_z(t)}{W}, \tag{4.9}$$

which follows from relations (4.3). Then, we obtain integral (4.7) and similar integrals. Substituting the result and expressions (4.8) into (3.9), we arrive at the following equation for describing the evolution of supersaturation:

$$-(\beta C)^{-1}\frac{dC}{dt} = N_S\{2(z_0 + \lambda_z)[V(\xi_0 + \lambda_\xi) + U(\eta_0 + \lambda_\eta)] + W\cot\varphi[(\xi_0 + \lambda_\xi)^2 + (\eta_0 + \lambda_\eta)^2$$
$$+ 2(\xi_0 + \lambda_\xi)(\eta_0 + \lambda_\eta)/\cos\varphi]\} + \tan\varphi\{N_-[2U(x_0^- + \lambda_x)(z_0^- + \lambda_z) + W(x_0^- + \lambda_x)^2]$$
$$+ N_S[2U(x_0 + \lambda_x)(z_0 + \lambda_z) + W(x_0 + \lambda_x)^2]H[\lambda_x(t)(V/U - 1/\cos\varphi) - \xi_0]\}. \tag{4.10}$$

Here $\lambda_\xi = (\lambda_x - \lambda_y \cos\varphi)/\sin\varphi$ and $\lambda_\eta = (\lambda_y - \lambda_x \cos\varphi)/\sin\varphi$. It is obvious from (4.9) that Eq. (4.10) can be written as

$$-(\beta C)^{-1} dC/dt = A_0 + A_1\lambda_x + A_2\lambda_x^2 + (B_0 + B_1\lambda_x + B_2\lambda_x^2) H[\lambda_x(t)(V/U - 1/\cos\varphi) - \xi_0],$$

where the constants A_j and B_j ($j = 0$, 1, and 2) are obtained from (4.10) (for brevity they are not presented). Dividing the last equation by relation (4.3) for the function $\lambda_x(t)$ and integrating, we have the following relation between supersaturation and λ_x:

$$U(C_0 - C)/\beta = A_0\lambda_x + A_1\lambda_x^2/2 + A_2\lambda_x^3 + (B_0\lambda_x + B_1\lambda_x^2 + B_2\lambda_x^3) - (B_0 Z + B_1 Z^2 + B_2 Z^3),$$

$$\begin{cases} Z = \lambda_x & \text{for} \quad \lambda_x \leqslant \lambda_*, \\ Z = \lambda_* & \text{for} \quad \lambda_x > \lambda_*. \end{cases} \tag{4.11}$$

Here $\lambda_* = \xi_0/[V/U - 1/\cos\varphi]$. The solution of the problem will be completed when we substitute the cubic polynomial $C = C(\lambda_x)$ from (4.11) into the quadrature (4.3) (the first equation). This quadrature relates the parameter λ_x to time. All the remaining functions of interest, f, f_-, etc. are already expressed in terms of λ_x.

Among the distribution functions f, f_+, and f_- in the given simple example, the monodisperse [by virtue of the initial condition $f_0(x, y, z) = N_S\delta(x - x_0)\delta(y - y_0)\delta(z - z_0)$ and relation (4.2)] fraction described by the function f is of prime interest, because it defines the growth of the most "representative" crystals with all faces. The physical meaning of the parameter λ_* is that for $\lambda_x = \lambda_*$ this fraction reaches the boundaries of the region $y = x/\cos\varphi$, where some faces of the crystal disappear. The process continues up to complete elimination of supersaturation ($C = 0$). The monotonic character of relation (4.11) shows that supersaturation necessarily reaches zero at the point $\lambda_x = \lambda_k$. If $\lambda_* < \lambda_k$, during evolution the monodisperse fraction reaches a state with vanishing faces and then crystals with a cross section in the form of a regular k-gon will grow [here the fraction described by the function f_- (4.5) is also present]. If $\lambda_* > \lambda_k$, crystallization ceases without reaching the boundary of the region $y = x/\cos\varphi$. Naturally, in more complicated cases (under general additional conditions) analysis is more difficult to perform, although the main features of analysis are similar to a certain extent to the example considered above, and the physical meaning of some relations can be interpreted geometrically using the characteristics of Eq. (1.3) in the plane (x, y).

In conclusion, we make a few remarks. The determination of the growth rate of crystal faces is a separate problem, whose numerous aspects are topical at present [7, 8, 21]. The fact is that several mechanisms of crystal growth were substantiated theoretically, for example, "thermodynamic theories," "dislocation theories," etc. [7–9, 21]. It is also known [8, 21] that the growth rate of a face is markedly influenced by impurities. Furthermore, the same substance "acts" differently on different faces of the same crystal. Therefore, in practice, using a law for the growth rates of faces, one usually determines to which mechanism of crystal growth experimental data fit best of all. Then, one chooses coefficients in theoretical models, seeking agreement with experiment, and simultaneously takes into account "imperfections" of the course of the process that are difficult to control. Both theory and experiment [21] lead to different growth rates of different faces of crystals. In some cases, the difference in growth rate between faces can be very considerable. Thus, Linnikov [22] established that the growth rates of two types of faces of calcium sulfate (gypsum) crystals (in meters per second) differ by about two orders of magnitude and are defined by the formulas

$$V_1 = 67{,}982(C - C_*)^2 \exp\left[-\frac{(61.147 \pm 19.031)\cdot 10^3}{RT}\right],$$

$$V_2 = 29{,}424 \frac{C^2}{(RT)^2 \ln^2(C/C_*)} \exp\left[-\frac{(15.40 \pm 3.56)\cdot 10^3}{(RT)^2 \ln(C/C_*)}\right],$$

which were obtained using the procedure described above.

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