MATHEMATICAL MODELING OF CRYSTAL GROWTH WITH ALLOWANCE FOR MEIRS KINETICS

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Abstract—The process of nucleation and growth of crystals in a metastable medium (supercooled liquid or supersaturated solution) is studied theoretically in the presence of Meirs kinetics. The removal of crystals and their "diffusion" in the space of radii are taken into account in the Fokker-Planck equation for the distribution function. The time-dependent external heat (or mass) flux which controls the level of system metastability is included in the heat (mass) balance equation. A complete analytical solution of integro-differential model is obtained.

Index Terms— Crystallizer, distribution function, kinetics, nucleation.

I. INTRODUCTION

Industrial production of different materials from metastable systems plays an important role in metallurgy, materials physics, chemical industry, production of food and drugs [1-3]. Every process of industrial crystallization should provide obtaining crystals of a given structure and properties (shape, size and composition). This aim can be achieved on the basis of different mechanisms of nucleation and crystal growth. In the case of industrial crystallizers, they highly depend on the crystal withdrawal rate, the rate of metastability (supercooling or supersaturation) reduction as well as on the rate of external heat (or mass) fluxes. A deeper understanding of these phenomena is required for the control and design of crystallization products. Note that such processes are described by a nonlinear system of integro-differential equations. This is why the methods of its solution are poorly elaborated.

The present work is concerned with a mathematical description of the phase transition process in a crystallizer when the kinetic equation takes into account the crystal withdrawal rate and the balance equation contains the heat (mass) source term. This model reflects the real nucleation and growth processes in industrial crystallizers and the analytical solution obtained represents the novelty of the current studies.

II. THE MODEL

The distribution function f accounting for the particle fluctuations and crystal withdrawal rate takes the form [4,5]

$$\frac{\partial f}{\partial \tau} + \frac{\partial}{\partial r}(gf) + h(r)f = \frac{\partial}{\partial r}\left(D\frac{\partial f}{\partial r}\right), \quad r > r_*. \quad (1)$$

Here r and τ are the spatial and time variables, function $h(r)$ describes the crystal withdrawal rate and r_* is the critical radius of crystals. The exact form of coefficient D is a hard task of statistical physics. However, for the sake of simplicity, one can use the following approximation [4]

$$D = d_1 g(\tau, r) = d_1 \frac{dr}{d\tau}, \quad (2)$$

where d_1 is a constant coefficient.

The growth rate g of particles for the kinetic regime can be expressed as [6]

$$g(\tau) = g(\Delta C) = \beta_* \Delta C = G(C), \quad (3)$$

$$g(\tau) = g(\Delta\Theta) = \beta_* \Delta\Theta = G(\Theta), \quad (4)$$

where ΔC (or $\Delta\Theta$) are the supersaturation (or supercooling), C (or Θ) are the current concentration of impurity (or temperature).

Let us assume that the coefficient h is constant [7]

$$h = \frac{q}{V}, \quad 0 \le r \le r_p, \quad (5)$$

where q and V are the feed rate and total volume, r_p is the radius of product crystals.

Taking into account expressions (3)-(5) we rewrite the kinetic equation (1) in the form

$$\frac{\partial f}{\partial \tau} + G(C)\frac{\partial f}{\partial r} + hf = d_1 G(C)\frac{\partial^2 f}{\partial r^2}. \quad (6)$$

The mass (heat) balance equations can be written as

$$\frac{dC}{d\tau} = Q_C - 4\pi C_p \int_{r_*}^{\infty} r^2 \left(f(r,\tau)\frac{dr}{d\tau} - D\frac{\partial f}{\partial r}\right) dr, \quad (7)$$

$$\rho_m C_m \frac{d\Theta}{d\tau} = Q_\Theta + 4\pi L_V \int_{r_*}^{\infty} r^2 \left(f(r,\tau)\frac{dr}{d\tau} - D\frac{\partial f}{\partial r}\right) dr, \quad (8)$$

where L_V is the latent heat of solidification, C_p is the concentration at saturation, ρ_m and C_m are the density and heat capacity, Q_C and Q_Θ are the external mass and heat fluxes.

Next we use the single designation $\Delta C(t) = C(t) - C_p$ for concentration and temperature problems.

We assume that the initial distribution function and supersaturation are known

$$f = f_0(r), \tau = 0, \quad (9)$$

$$\Delta C = \Delta C_0, \tau = 0. \quad (10)$$

The first boundary condition for the distribution function takes the form [8]

$$gf - D\frac{\partial f}{\partial r} = I(\Delta C), \quad r = r_*, \quad \tau > 0 \quad . \quad (11)$$

The nucleation rate I is assumed in the Meirs form

$$I = I_*(\Delta C)^p. \quad (12)$$

Here I_* and p are empirical constants.

The second boundary condition for the distribution function is

$$f = 0, \quad r = r_p. \quad (13)$$

Let us introduce the following dimensionless parameters

$$w(t) = \frac{\Delta C}{\Delta C_0}, \quad b_1 = \frac{4\pi C_p}{\Delta C_0}, \quad Q = \frac{Q_C \tau_0}{\Delta C_0}, \quad I_0 = \left(\frac{\beta_* \Delta C_0}{I_0}\right)^{1/4},$$

$$\tau_0 = \left(\beta_*{}^3 \Delta C_0{}^3 I_0\right)^{-1/4}, F_0 = I_0{}^4 f_0, \quad F = I_0{}^4 f, \quad (14)$$

$$u_0 = \frac{d_1}{l_0}, \quad t = \frac{\tau}{\tau_0}, \quad s = \frac{r}{l_0}, s_p = \frac{r_p}{l_0}, \quad s_* = \frac{r_*}{l_0},$$

$$x = s - s_*, \ \gamma = \tau_0 h, \quad I_0 = I(\Delta C_0).$$

These parameters should be replaced for supercooled systems as:

$$w(t) = \frac{\Delta\Theta}{\Delta\Theta_0}, \quad b_1 = \frac{4\pi L_V}{\rho_m c_m \Delta\Theta_0}, \quad Q = -\frac{Q_\Theta \tau_0}{\rho_m c_m \Delta\Theta_0}, \quad (15)$$

$$\tau_0 = \left(\beta_*{}^3 \Delta\Theta_0{}^3 I_0\right)^{-1/4}, \quad I_0 = \left(\frac{\beta_* \Delta\Theta_0}{I_0}\right)^{1/4}.$$

The kinetic equation (6), the initial condition (9) and the boundary conditions (11) and (13) in the dimensionless variables (14) take the form:

$$\frac{\partial F}{\partial t} + w\frac{\partial F}{\partial x} + \gamma F = u_0 w \frac{\partial^2 F}{\partial x^2}, \quad t > 0, \quad 0 < x < x_0, \quad (16)$$

$$F(x, 0) = F_0(x), \quad (17)$$

$$F - u_0 \frac{\partial F}{\partial x} = [w(t)]^{p-1}, \quad x = 0, \quad (18)$$

$$F = 0, \quad x = x_0, \quad (19)$$

where $x_0 = s_p - s_*$.

The mass (heat) balance equations (7), (8) can be written in dimensionless variables (14) as

$$\frac{dw}{dt} = Q(t) - b_1 w \int_0^{x_0} F(x,t)(x + s_*)^2 dx + P(x,t), \quad (20)$$

$$P = b_1 w u_0 \int_0^{x_0} (x + s_*)^2 \frac{\partial F}{\partial x} dx,$$

$$w = 1, t = 0.$$

III. STATIONARY PROCESS OF CRYSTALLIZATION

If the distribution function F_s is independent of time, equations (16), (18), (19) take the form:

$$w_s \frac{dF_s}{dx} + \gamma F_s = u_0 w_s \frac{d^2 F_s}{dx^2}, \quad 0 < x < x_0, \quad (21)$$

$$F_s - u_0 \frac{dF_s}{dx} = w_s^{p-1}, \quad x = 0, \quad (22)$$

$$F_s = 0, \quad x = x_0. \quad (23)$$

After solving the system (21) - (23), we can find

$$F_s(x) = \exp\left(\frac{x}{2u_0}\right)[C_1 \exp(kx) + C_2 \exp(-kx)], \quad (24)$$

$$C_1 = \frac{-2w_s^{p-1}\exp(-2kx_0)}{1-\exp(-2kx_0)+2ku_0(1+\exp(-kx_0))},$$

$$C_2 = \frac{2w_s^{p-1}}{1-\exp(-2kx_0)+2ku_0(1+\exp(-kx_0))},$$

$$k = \sqrt{\frac{\gamma}{u_0 w_s} + \frac{1}{4u_0^2}}.$$

Now substituting the distribution function (24) into the balance condition (20), we have

$$Q_s = b_1 w_s \int_0^{x_0} (x + s_*)^2 R(x) dx, \quad (25)$$

$$R(x) = -\exp\left(\frac{x}{2u_0}\right)\left[ku_0(C_1 \exp(kx) - C_2 \exp(-kx)) - \frac{1}{2}(C_1 \exp(kx) - C_2 \exp(-kx))\right] .$$

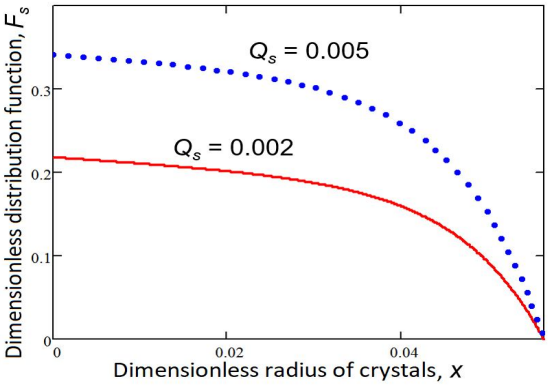


Fig.1. The steady-state distribution function at different thermal (mass) fluxes Q_s: $w_s = 0.225$ (solid line), $w_s = 0.349$ (dotted line).

Table I. Physical parameters.

Quantity	Value	Units
$\Delta\Theta_0$	20	°C
L_V	$7{\cdot}10^9$	J m^{-3}
ρ_m	$7{\cdot}10^3$	kg m^{-3}
I_0	10^9	m^{-3} s^{-1}
C_m	840	J kg^{-1} °C^{-1}
β_*	$0.5{\cdot}10^{-7}$	m s^{-1} °C^{-1}
h	$4{\cdot}10^{-3}$	s^{-1}
r_p	10^{-5}	m
r_*	10^{-9}	m
p	2	-
u_0	10^{-2}	-
F_0	0	-

Fig. 1 illustrates the dimensionless distribution function in accordance with expressions (24) and (25). The physical parameters are listed in Table I [6]. Note that a larger amount of crystals appear at larger supercooling. Let us consider below more actual unsteady-state case frequently met in practice.

IV. NONSTATIONARY PROCESS OF CRYSTALLIZATION

In order to solve the problem (16)-(19) by means of the method of separation of variables, one can transform the boundary condition (18) into the homogeneous form. To do this, let us introduce the following function

$$F(x,t) = F_1(x,t) + \frac{K(t)(x_0-x)}{x_0+u_0}, \quad K(t) = [w(t)]^{p-1}. \tag{26}$$

Taking this into account, the problem (16)-(19) becomes

$$\frac{\partial F_1}{\partial t} + w\frac{\partial F_1}{\partial x} + \gamma F_1 - u_0 w\frac{\partial^2 F_1}{\partial x^2} = \nu(x,t), \tag{27}$$

$$F_1(x,0) = F_0(x) - \frac{x_0-x}{x_0+u_0}, \tag{28}$$

$$F_1 - u_0\frac{\partial F_1}{\partial x} = 0, \quad x = 0, \tag{29}$$

$$F_1 = 0, \quad x = x_0, \tag{30}$$

where

$$\nu(x,t) = \frac{K(t)}{x_0+u_0}\big(w(t) - \gamma(x_0-x)\big) - \frac{x_0-x}{x_0+u_0}\frac{dK}{dt}. \tag{31}$$

Setting

$$F_1(x,t) = X(x)T(t) \tag{32}$$

and taking into account that

$$X(0) - u_0X'(0) = 0, \quad X(x_0) = 0, \tag{33}$$

we obtain eigenfunctions $X_k(x)$ and eigenvalues n_k from equation (27)

$$X_k(x) = \exp\left(\frac{x}{2u_0}\right)(2n_ku_0\cos(n_kx) + \sin(n_kx)), \tag{34}$$

$$2n_ku_0\cos(n_kx_0) + \sin(n_kx_0) = 0, \quad k = 0,1,2,\ldots \tag{35}$$

Expanding functions $\nu(x,t)$ and $F_1(x,0)$ in series in eigenfunctions $X_k(x)$, we get the following solution of homogeneous problem

$$\nu(x,t) = \sum_{k=0}^{\infty}\nu_k(t)X_k(x), \tag{36}$$

$$F_1(x,0) = \sum_{k=0}^{\infty}F_{0k}X_k(x), \tag{37}$$

$$\nu_k(t) = \frac{1}{I_k}\int_0^{x_0}\nu(x,t)\exp\left(-\frac{x}{u_0}\right)X_k(x)dx, \tag{38}$$

$$F_{0k} = \frac{1}{I_k}\int_0^{x_0}\left(F_0(x) - \frac{K(0)(x_0-x)}{x_0+u_0}\right)\exp\left(-\frac{x}{u_0}\right)X_k(x)dx, \tag{39}$$

$$I_k = \int_0^{x_0}(2n_ku_0\cos(n_kx) + \sin(n_kx))^2\,dx. \tag{40}$$

Substituting this solution into (32), we get the unknown function

$$F_1(x,t) = \sum_{k=0}^{\infty}X_k(x)T_k(t). \tag{41}$$

Now combining expressions (27), (36), (37) and (41), we get the following equation for $T_k(t)$:

$$\frac{dT_k}{dt} + \mu_k(t)T_k(t) = \nu_k(t), \tag{42}$$

$$\mu_k = w(t)\left(n_k^2u_0 + \frac{1}{4u_0}\right) + \gamma.$$

Next integrating (42) and substituting the result into (41), we obtain

$$F_1(x,t) = \sum_{k=0}^{\infty}\left(F_{0k} + \int_0^t\nu_k(t_1)\exp\left(\int_0^{t_1}\mu_k(t_2)dt_2\right)dt_1\right)\cdot \exp\left(-\int_0^t\mu_k(t_2)dt_2\right)X_k(x).$$

Now dependence (26) is determined as a function of supersaturation (supercooling) $w(t)$, which will be found below. The mass (heat) balance equation in dimensionless variables has the form of equation (20), where

$$P = b_1wu_0\int_0^{x_0}(x+s_*)^2\left[\frac{\partial F_1}{\partial x} - \frac{w^{p-1}}{x_0+u_0}\right]dx.$$

At first, let us find the integral term in equation (20)

$$F_1(x,t) = \sum_{k=0}^{\infty}\exp(-\xi_k(t))X_k(x)\left(F_{0k} + \int_0^t\nu_k(t_1)\exp(\xi_k(t_1))\,dt_1\right), \tag{43}$$

$$\xi_k(t) = \frac{S_k(t)}{4u_0},$$

$S_k(t) = (1 + 4u_0^2 n_k^2)\int_0^t w(t_1)dt_1 + 4u_0\gamma t.$

As the derivative $S'(t) > 0$, function $S(t)$ increases and its maximum attains at the upper integral limit. Let us estimate the integral contribution in equation (43) by means of the saddle-point method for the Laplace-type integral [9]. Keeping in mind only the main contribution in the asymptotic expansion, we arrive at

$$\int_0^t \nu_k(t_1)\exp\left(\frac{S_k(t_1)}{4u_0}\right)dt_1 \approx \frac{4u_0\nu_k(t)\exp\left(\frac{S_k(t)}{4u_0}\right)}{S_k'(t)}. \quad (44)$$

Combining expressions (43) and (44), we come to

$$F_1 \approx \sum_{k=0}^{\infty} X_k(x)\left(F_{0k}\exp(-\xi_k(t)) + \frac{4u_0\nu_k(t)}{(1+4u_0^2n_k^2)U'(t)+4u_0\gamma}\right), \quad (45)$$

$$U(t) = \int_0^t w(t_1)dt_1.$$

Now substitution F_1 from (45) into (20) leads to the following Cauchy problem

$$\begin{cases} U'' = M(U, U', t) \\ U = 0,\ U' = 1,\ t = 0 \end{cases}, \quad (46)$$

$$M = \left(Q(t) - b_1 U'^p \Psi - b_1 U' S_2 - 4u_0 b_1 U'(U'^p S_3 - U'^{p-1} S_4) + \delta_1 U'^p\right)\cdot(1 - b_1 U'^{p-1} S_1)^{-1},$$

$$\Psi = \frac{(x_0+s_*)^4 - 4s_*^3(x_0+s_*) + 3s_*^4}{12(x_0+u_0)},$$

$$\delta_1 = -\frac{b_1 u_0}{x_0+u_0}\left[\frac{(x_0+s_*)^3}{3} - \frac{s_*^3}{3}\right],$$

$$S_1 = \sum_{k=0}^{\infty} 4u_0\nu_{k3}\frac{Z_k - u_0 Y_k}{\Phi_k},$$

$$S_2 = \sum_{k=0}^{\infty} F_{0k}\exp(-\xi_k(U))(Z_k - u_0 Y_k),$$

$$S_3 = \sum_{k=0}^{\infty} \nu_{k1}\frac{Z_k - u_0 Y_k}{\Phi_k}, \quad S_4 = \sum_{k=0}^{\infty} \nu_{k2}\frac{Z_k - u_0 Y_k}{\Phi_k},$$

$$Z_k = \int_0^{x_0} X_k(x)(x + s_*)^2 dx,$$

$$Y_k = \int_0^{x_0} (x + s_*)^2\left(\frac{dX_k}{dx}\right)dx,$$

$$\Phi_k(U') = (1 + 4u_0^2 n_k^2)U'(t) + 4u_0\gamma,$$

$$\nu_{k1} = \frac{1}{I_k}\int_0^{x_0}\frac{X_k(x)\exp\left(-\frac{x}{u_0}\right)dx}{x_0+u_0},$$

$$\nu_{k2} = \frac{\gamma}{I_k}\int_0^{x_0}\frac{(x_0-x)X_k(x)\exp\left(-\frac{x}{u_0}\right)dx}{x_0+u_0},$$

$$\nu_{k3} = \frac{(p-1)}{I_k}\int_0^{x_0}\frac{(x_0-x)X_k(x)\exp\left(-\frac{x}{u_0}\right)dx}{x_0+u_0}.$$

Thus the Cauchy problem (46) defines function $U(t)$, which gives the supersaturation $w(t) = U'(t)$ and the distribution function $F(x, t)$.

V. NUMERICAL EXAMPLES

Figs. 2, 3 demonstrate the dimensionless supersaturation and distribution function at constant external fluxes Q and $F_0(x) = (x_0 - x)/(x_0 + u_0)$. When increasing Q the system supersaturation w becomes greater for all values of time. The distribution function of crystals therewith becomes greater because desupersaturation caused by crystal growth decreases. Note that the distribution function of a given size of crystals shown in Fig. 3 monotonically decreases with increasing time, and smaller F corresponds to greater crystals.

Figs. 4 - 6 illustrate the unsteady-state regime at $Q(t) = A(1 - \cos(\omega t))$, $\omega = {}^{10\pi}/_{t_1}$, $t_1 = 150$. This regime describes a periodic scenario (when impurity comes to or heat goes out a crystallizer) that leads to an oscillatory behavior of decreasing supersaturation (supercooling) w. The distribution function plotted in Fig. 5, as before, decreases with time and size. In addition, this function, as is easily seen in Fig. 6, decreases with time in an oscillatory manner so that F is smaller for greater crystal sizes. What is more, when Q grows F builds up as is seen from Figs. 5(a) and 5(b) as well as from 6(a) and 6(b).

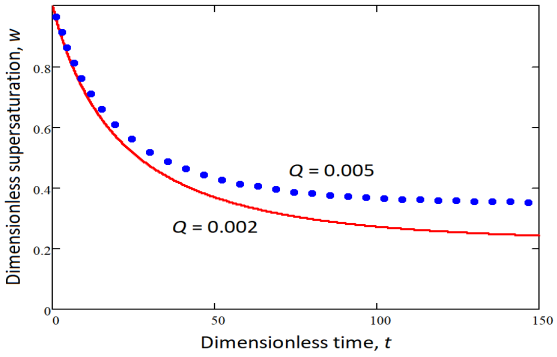
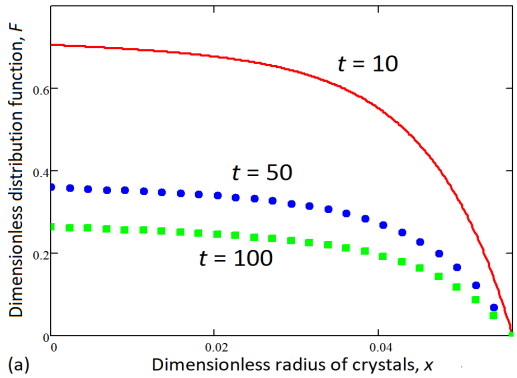


Fig. 2. Dimensionless supersaturation (supercooling) versus dimensionless time.



(a)

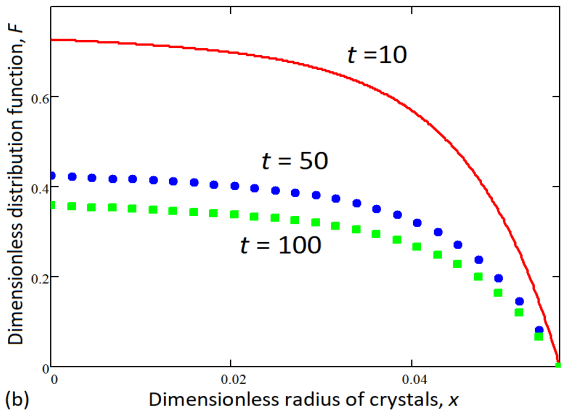


Fig. 3. Dimensionless distribution function versus dimensionless radius of crystals: Q = 0.002 (a) and Q = 0.005 (b).

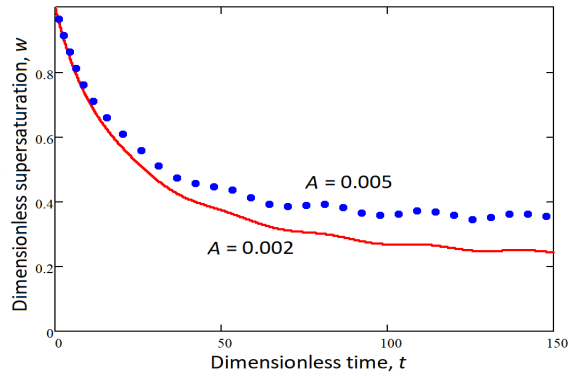
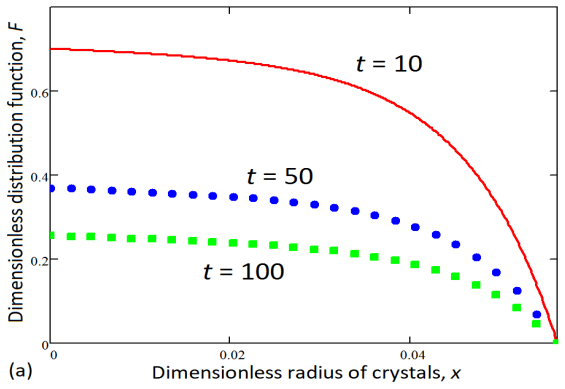


Fig. 4. Dimensionless supersaturation (supercooling) versus dimensionless time.



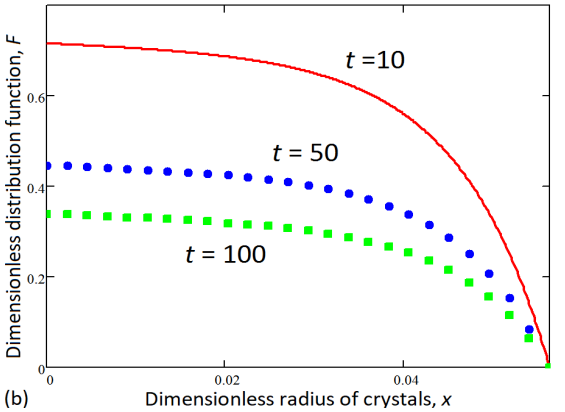
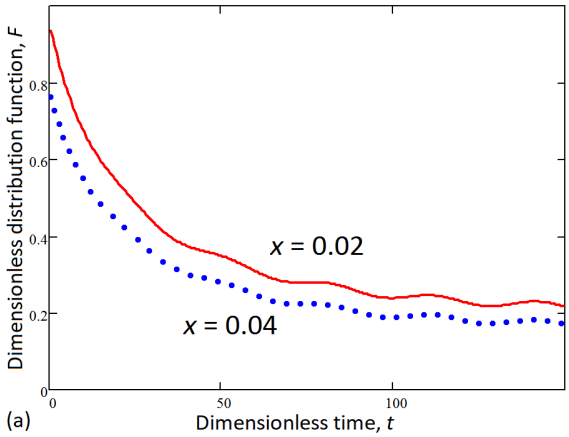


Fig. 5. Dimensionless distribution function versus dimensionless radius of crystals: A = 0.002 (a) and A = 0.005 (b).

Comparing Figs. 3(a) and 5(a) as well as 3 (b) and 5(b) one can note that the distribution functions in cases of constant and variable Q are very similar that is some oscillations in Q are smoothed in F due to the integral terms.



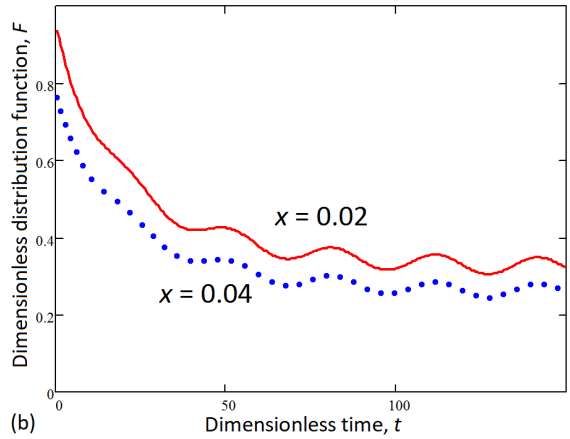


Fig. 6. Dimensionless distribution function versus dimensionless time: A = 0.002 (a) and A = 0.005 (b).

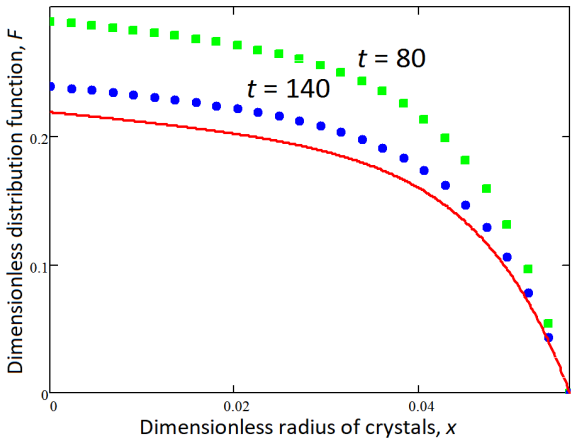


Fig. 7. Dimensionless distribution function versus dimensionless radius of crystals: Q = 0.002. The solid line shows the steady-state distribution function.

Fig. 7 represents relaxation dynamics of the distribution function which approaches to its steady-state solution (24) with time. This shows that the initial conditions do not play an important role at large times and a solution lying close to the

steady-state solution establishes.

CONCLUSION

In this paper, we study a simple nonstationary integro-differential model of industrial crystallizer with allowance for removal of crystals. Nucleation and evolution of crystallites in a supersaturated (supercooled) system is considered in accordance with the Meirs kinetic mechanism. The Fokker-Planck equation for the distribution function includes the "diffusion" term responsible for the "diffusion" of this function in space of crystal radii. A complete analytical solution of nonlinear unsteady-state problem is found on the basis of saddle-point method for the Laplace-type integral and separation of variables method. An exact analytical solution for the corresponding steady-state problem is found as well. It is shown that the supersaturation (supercooling) and the distribution function decrease with time.

As a final note, the theory under consideration can be extended to take into account more complicated dependencies of the “diffusion” coefficient D and growth rate g [10, 11].

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