

# Mathematical modeling of the stationary nucleation and crystallization process in supersaturated systems with a crystallizer

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**Abstract.** Motivated by important industrial applications we consider the growth process of solid particles in a supersaturated (supercooled) system with allowance for a crystallizer. The particle-radius distribution function satisfies the second order kinetic equation supplemented by different boundary conditions. An exact steady-state analytical solution is found. We show that two different types of analytical solutions for the kinetic equation exist.

## 1. Introduction

The process of growth of a new phase in metastable systems can be divided into three stages: nucleation, growth of critical nuclei and relaxation of a new phase to equilibrium. The division is conditional, because all these processes occur simultaneously. Modeling the processes of formation of a new phase is important both for fundamental research in the field of phase transitions and for industrial applications. The particle size distribution can have a decisive influence on the properties of the systems in the production of powder materials from melts, precipitation from solutions, synthesis of colloidal solutions and so on.

In this study, the process of formation and growth of particles of a new phase under stationary conditions is considered. Such conditions can be ensured when the particles of the solid phase are continuously removed from the liquid and the supersaturation (supercooling) is artificially maintained. The removal of particles can be realized both as a result of processes of precipitation of large particles due to sedimentation, fragmentation and sedimentation of large volumes of the new phase, and also due to artificial deposition, for example, during centrifugation.

The problem of stationary distribution was previously considered by Buevichi and Mansurov [1]. However, they considered the deterministic growth of solid crystals without their fluctuations. The present paper takes into account random processes in the Fokker-Planck equation for the particle-radius distribution function.

## 2. Model

It is assumed that the physical properties of both the solution and the crystals are independent of supersaturation (hereinafter, supersaturation will also be understood as supercooling) and time. Supersaturation is homogeneous throughout the reservoir volume. The nucleation kinetics is stationary. This is permissible as the time of nucleation process, as a rule, is several orders of



magnitude smaller than the time of continuous crystallization for any real supersaturation. The size of spherical crystals is determined by using one parameter, their radius.

The crystal radius is a random variable satisfying the stochastic equation [2]

$$dr = g(t, r)dt + \sqrt{2D}W, \quad (1)$$

where  $t$  is the growth time,  $g(t, r)$  is the growth rate of a particle that has no oscillations,  $D$  is a function that expresses the speed of free oscillations (the coefficient of mutual Brownian diffusion of a particle) and  $W$  is the Wiener process. The distribution function  $f$  of particles of radius  $r$  for the stochastic equation (1) considering the crystallizer (crystal derivation) is described by a kinetic equation of the Fokker-Planck type [3].

$$\frac{\partial f}{\partial t} + \frac{\partial}{\partial r}(gf) + h(r)f = \frac{\partial}{\partial r} \left( D \frac{\partial f}{\partial r} \right), \quad r > r_*. \quad (2)$$

The function  $h(r)$  describes the rate of crystal extraction,  $r_*$  is a critical radius. The exact definition of  $D$  is a difficult problem in statistical physics. However, in the first approximation one can assume that  $D$  is proportional to the nucleation rate of growth [3, 4]

$$D = d_1 g(t, r), \quad (3)$$

where  $d_1$  is a coefficient.

The rate of particle growth  $g$  can be found from a problem of the Stefan type in a metastable system [4, 5]. The result can be expressed in the form

$$g(t, r) = \frac{\beta_* \Delta \theta}{1 + \beta_* q r}, \quad q = \frac{L_V}{\lambda_l} \quad (4)$$

if the system is a supercooled melt and in the form

$$g(t, r) = \frac{\beta_* \Delta C}{1 + \beta_* q r}, \quad q = \frac{C_p}{D_l} \quad (5)$$

if the system is a supersaturated solution. Here,  $\beta_*$  is the kinetic coefficient,  $\lambda_l$  and  $D_l$  are the temperature conductivity and diffusion coefficients,  $\Delta C$  is the supersaturation,  $\Delta \theta$  is the supercooling. The heat (mass) balance equation for the dimensionless supercooling  $W = \Delta \theta / \Delta \theta_0$  (supersaturation  $W = \Delta C / \Delta C_0$ ) can be written as [4].

$$w(\tau) = 1 - b \int_{r_*}^{\infty} r^3 f(\tau, t) dr, \quad \tau > 0, \quad (6)$$

where  $b = 4\pi L_V / (3\rho_m C_m \Delta \theta_0)$  if the system under consideration is a supercooled melt, and  $b = 4\pi C_p / (3 \Delta C_0)$  if the system is represented by a supersaturated solution. Here  $L_V$  is the latent heat parameter,  $C_p$  is the concentration at saturation,  $\rho_m$  and  $C_m$  are the density and specific heat of the mixture and subscript 0 designates the initial state.

For a complete investigation of the problem, it is necessary to set the initial and boundary conditions. As the initial condition for the distribution function, it is usually assumed that there are not nuclei in the system:

$$f = 0, \quad \tau = 0. \quad (7)$$

The initial condition for  $w$  becomes

$$w = 1, \quad \tau = 0. \quad (8)$$

The first boundary condition for the density distribution function takes the form

$$gf - D \frac{\partial f}{\partial r} = I(w), \quad r = r_*, \quad \tau > 0. \quad (9)$$

The empirical expressions for the nucleation rate which are frequently used in analyzing many industrial processes can be expressed as

$$I = I_*(\Delta\theta)^p = (I_*(w \Delta \theta_0))^p \quad (10)$$

for supercooled melts and

$$I = I_*(\Delta C)^p = (I_*(w \Delta C_0))^p \quad (11)$$

for supersaturated solutions. Expressions (10) and (11) are frequently called the Meirs nucleation kinetics. It follows from the normalization condition that the distribution function vanishes for sufficiently large  $r$ .

Generally speaking, two boundary conditions are possible. The first of them reflecting the distribution function decaying is

$$f = 0, \quad r \rightarrow \infty. \quad (12)$$

The second one describes the case when the density distribution function vanishes for a finite  $r$

$$f = 0, \quad r = r_0. \quad (13)$$

### 3. Steady-state regime

We are dealing with two processes: the formation and growth of crystals and their removal. These processes can balance each other. Thus, if the supersaturation is artificially maintained, it is possible to achieve the existence of a solution in the form of a stationary (time-independent) distribution-density function. The equation becomes an ordinary differential equation, and the initial conditions are no longer required. In this paper, we assume that the rate of the crystal removal is independent of their radii. The experiment shows that the crystal growth rate  $g$  is frequently constant. In this case, the kinetic equation takes the form

$$D \frac{d}{dr} \left( \frac{df}{dr} \right) - g \frac{d}{dr}(f) - hf = 0, \quad (14)$$

$$\frac{d}{dr} \left( \frac{df}{dr} \right) - A \frac{d}{dr}(f) - Bf = 0, \quad A = \frac{g}{D}, \quad B = \frac{h}{D}. \quad (15)$$

The solution of this equation has the form

$$f = C_1 e^{\lambda_1 r} + C_2 e^{\lambda_2 r}, \quad (16)$$

$$\lambda_1 = \frac{A + \sqrt{(A^2 + 4B)}}{2}, \quad \lambda_2 = \frac{A - \sqrt{(A^2 + 4B)}}{2}, \quad (17)$$

where  $C_1$  and  $C_2$  are determined from the boundary conditions, consequently two cases are possible.

In the first case, (12), we have

$$C_1 = 0, \quad (18)$$

$$C_2 = \frac{I}{g(1 - d_1 \lambda_2) e^{\lambda_2 r_*}}. \quad (19)$$

In the second case, (13), we get

$$C_1 = -\frac{Ie^{\lambda_2 r_0}}{g((d_1 \lambda_1 - 1)e^{\lambda_2 r_0} e^{\lambda_1 r_*} - (d_1 \lambda_2 - 1)e^{\lambda_1 r_0} e^{\lambda_2 r_*})}, \quad (20)$$

$$C_2 = \frac{Ie^{\lambda_1 r_0}}{g((d_1 \lambda_1 - 1)e^{\lambda_2 r_0} e^{\lambda_1 r_*} - (d_1 \lambda_2 - 1)e^{\lambda_1 r_0} e^{\lambda_2 r_*})}. \quad (21)$$

The analytical solutions (16)-(21) can be rewritten in the dimensionless form as

$$F(x) = \frac{f}{C_2} = Ce^{\mu_1 x} + e^{\mu_2 x}, \quad (22)$$

$$C = \frac{C_1}{C_2}, \quad x = \frac{r}{d_1}, \quad \Lambda = \frac{4B}{A^2}, \quad (23)$$

$$\mu_1 = \frac{1}{2} \left( 1 + \sqrt{1 + \frac{4B}{A^2}} \right), \quad \mu_2 = \frac{1}{2} \left( 1 - \sqrt{1 + \frac{4B}{A^2}} \right). \quad (24)$$

Here the reduced constant  $C$  is introduced as

$$C = 0 \quad (25)$$

in the case of boundary conditions (18), (19) and

$$C = -e^{(\mu_2 - \mu_1)x_0} \quad (26)$$

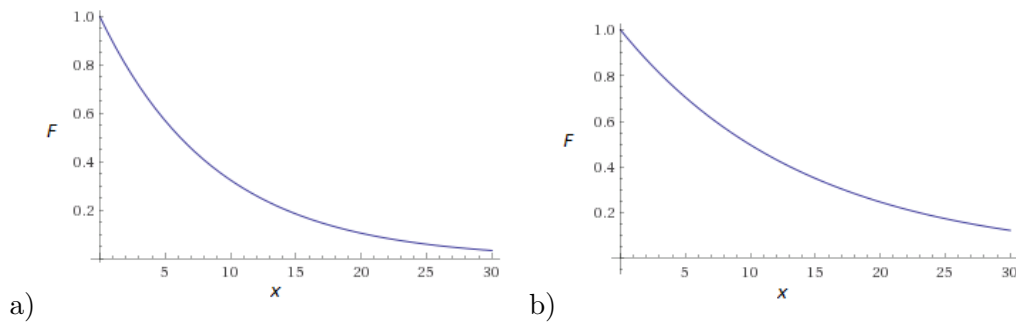
in the case of boundary conditions (20), (21).

#### 4. Conclusions

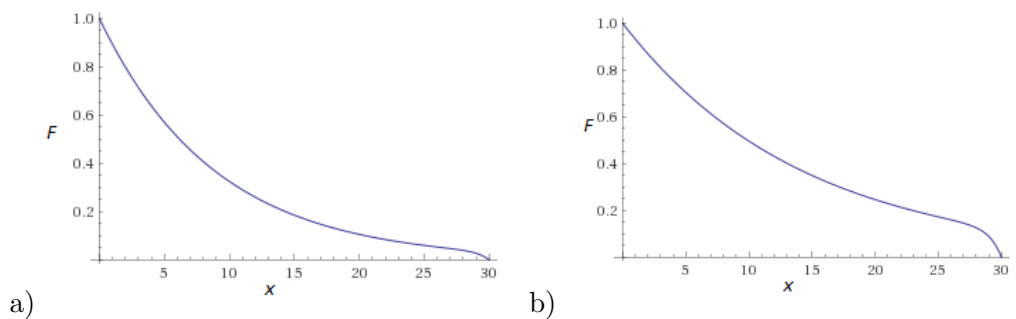
Figures 1 and 2 show graphs of the distribution function for different boundary conditions. Of special interest is the case when the distribution function vanishes for finite  $r = x_0 d_1$ . As we can see, the function  $F$  in Figures 1 and 2 does not have extremal points and is a monotonically decreasing function. Thus, we come to the conclusion that under stationary conditions with increasing radius of the nuclei the probability of finding such nuclei in the crystallizer decreases. The difference between two boundary conditions (12) and (13) shown in Figures 1 and 2 consists in the fact that  $F = 0$  at  $x = x_0$  in Figure 2 while  $F \rightarrow 0$  at  $x \rightarrow \infty$  in Figure 1. This is connected with different boundary conditions (12) and (13) initially used in our model. Generally speaking, both of them are possible if the system approaches to its steady-state. This, in turn, depends, first of all, on system equilibria and how it tends to them. It depends on the level of system supercooling (supersaturation) as well. In addition, Figure 2 demonstrates the presence of inflection points appearing as a result of the boundary condition (13).

Note that increasing  $\Lambda$  (withdrawal rate  $h$ ) decreases the distribution function and the number of crystals as is seen from comparison of the left and right panels in Figures 1 and 2.

The distribution function behavior illustrated in Figures 1 and 2 is a direct consequence of the second spatial order of the kinetic equation (2) and corresponding boundary conditions. Indeed, if we are dealing with the first order kinetic equation the distribution function breaks down at a finite crystal radius [6, 7]. An important point is that the distribution function (22) is always decreasing because its second derivative is negative at any  $x$ .



**Figure 1.** Dimensionless distribution function versus dimensionless crystal radius at a)  $\Lambda = 0.5$  and b)  $\Lambda = 0.3$  plotted for the case of boundary condition (12).



**Figure 2.** Dimensionless distribution function versus dimensionless crystal radius at a)  $\Lambda = 0.5$  and b)  $\Lambda = 0.3$  plotted for the case of boundary condition (13),  $x_0 = 30$ .

## 5. References

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