

RESEARCH ARTICLE

Mathematical modeling of crystallization process from a supercooled binary melt

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The article is concerned with the analytical solution to the integro-differential system of balance and kinetic equations that describe the crystal growth phenomenon in a binary system for various nucleation kinetics. The effect of impurity concentration on the evolutionary behavior of crystals is shown. The nonlinear dynamics of a supercooled binary melt is studied with allowance for the withdrawal mechanism of product crystals from a metastable liquid of the crystallizer.

KEYWORDS:

nucleation, phase transformations, mathematical modeling

1 | INTRODUCTION

The phase and structural transitions occurring from metastable and nonequilibrium states underlie various physical processes and natural phenomena. These include, for example, the processes of freezing of water in nature,^{1–5} solidification of melts in metallurgy and lava in magma chambers,^{6–11} the growth of crystals from supersaturated solutions in the chemical industry and medicine.^{12–18}

The processes of nucleation and growth of crystallites occur at high supersaturation or supercooling of the liquid, when small elements of the new phase appear on tiny inclusions (impurities), grow and reduce the metastability degree of the liquid (solution or melt). As this takes place, at the initial stages, the growth of crystals occurs independently of each other due to the small size of the nucleating particles.^{19–21} When growing in supersaturated solutions, crystals decrease the supersaturation of the surrounding solution. When crystals grow in supercooled melts, they emit latent heat of crystallization, which compensates for the liquid supercooling. Thus, the supersaturation (or supercooling) of liquid decreases with time and the number and size of evolving crystals increase.^{22–24} In the later stages of the process, when the degree of liquid metastability is almost completely removed, and the number of crystals is large, they can interact with each other using processes such as coagulation, Ostwald ripening and fragmentation.^{25–30}

Since at different stages of phase transitions the evolving system of crystals is controlled by different physical processes, the mathematical models of such processes differ for different stages. Thus, for example, at the intermediate stage of phase transformation, nucleation and crystal growth are controlled by the kinetic equation for the particle size distribution function and the balance equation for heat (or impurity concentration). In this case, collisions, mergers, and decay of particles are not taken into account. At the next final stage of the phase transformation, such processes become possible and the mathematical model becomes much more complicated. The kinetic equation, for example, should take into account the possibility of coagulation and/or fragmentation of particles when their concentration in a metastable liquid becomes high.

Since each individual mathematical model is an integro-differential system of equations with moving boundaries of growing crystals, there are no general methods for solving such problems. Each separate statement of the problem requires the development of individual approaches to the solution, usually based on the development of approximate methods of analysis of the mathematical model. In this work, we develop the theory of nucleation and crystal growth in a metastable binary melt, where

the evolution of crystallites is controlled simultaneously by the temperature and concentration fields. The mathematical model of the process also takes into account the presence of a crystallizer, i.e. processes such as removal of product crystals from a metastable melt, impurity inflow, and heat removal in balance equations. Our approximate analytical theory is based on the previously developed theories^{31–33} of crystal growth in pure melts, as well as on the saddle point method for the Laplace-type integrals.³⁴

2 | THE MODEL

Let us assume that the melt supercooling is uniform throughout the entire volume of the crystallizer. In addition, we assume that the time and spatial coordinates do not affect the physical properties of the liquid and solid phases. Considering a binary system, the heat and mass balance equations can be written as

$$\rho_m C_m \frac{d\theta_l}{d\tau} = Q_\theta + 4\pi\rho_s L \int_{r_*}^{r_p} r^2 \left(f(r, \tau) \frac{dr}{d\tau} - D \frac{\partial f}{\partial r} \right) dr, \quad \tau > 0, \quad (1)$$

$$\frac{d\sigma_l}{d\tau} = Q_\sigma + 4\pi\sigma_l(1 - k_0) \int_{r_*}^{r_p} r^2 \left(f(r, \tau) \frac{dr}{d\tau} - D \frac{\partial f}{\partial r} \right) dr, \quad \tau > 0, \quad (2)$$

where θ_l and σ_l represent the temperature of a supercooled melt and the concentration of impurity, ρ_m and C_m are the mixture density and specific heat of the melt, L is the latent heat, ρ_s designate the solid phase density, Q_θ and Q_σ are the external mass and heat fluxes, k_0 is the impurity distribution factor, $\tau > 0$ is time, r is the radial coordinate of growing crystals, f is the distribution function, $dr/d\tau = g$ is the particle growth rate, r_* is the radius of critical nuclei, r_p is the radius of particles removed from the crystallizer (product crystals), and D is a function representing the rate of particle fluctuations. To simplify the matter let us consider that D is proportional to the growth rate²⁵ $D = d_1 dr/d\tau = d_1 g = d_1 \beta_* \Delta\theta$, where d_1 is a pertinent factor, β_* is the kinetic coefficient, $\Delta\theta = \theta_* - \theta_l - m\sigma_l$ is the supercooling, and m is the liquidus slope.

The Fokker-Planck equation determines the crystal size distribution function f :

$$\frac{\partial f}{\partial \tau} + \frac{\partial}{\partial r} \left(\frac{dr}{d\tau} f \right) + h(r)f = \frac{\partial}{\partial r} \left(D \frac{\partial f}{\partial r} \right), \quad r > r_*, \quad \tau > 0. \quad (3)$$

Here $h(r)$ is the crystal removal rate. For simplicity, we assume that h is constant. The system of equations (1)-(3) must be supplemented with the initial and boundary conditions

$$\Delta\theta = \Delta\theta_0, \quad \theta_l = \theta_0, \quad \sigma_l = \sigma_0, \quad f = f_0(r), \quad \tau = 0, \quad (4)$$

$$\frac{dr}{d\tau} f - D \frac{\partial f}{\partial r} = I(\Delta\theta), \quad r = r_*; \quad f = 0, \quad r = r_p. \quad (5)$$

Here the frequency of nucleation I has the form¹⁸

$$I = I_* \begin{cases} \exp(-p\Delta\theta_0^2/\Delta\theta^2) \\ (\Delta\theta)^p \end{cases}.$$

Note that the first line defines the Weber-Volmer-Frenkel-Zeldovich kinetics while the second one describes the Meirs kinetics.

For convenience, we introduce the following dimensionless variables:

$$\begin{aligned} F_0 = l_0^4 F_0, \quad F = l_0^4 F, \quad t = \frac{\tau}{\tau_0}, \quad s = \frac{r}{l_0}, \quad s_p = \frac{r_p}{l_0}, \quad s_* = \frac{r_*}{l_0}, \quad u_0 = \frac{d_1}{l_0}, \quad w = \frac{\Delta\theta}{\Delta\theta_0}, \quad T = \frac{\Delta\theta_l}{\Delta\theta_0}, \quad C = \frac{\Delta\sigma_l}{\Delta\sigma_0}, \\ b_1 = \frac{4\pi L}{\rho_m C_m \Delta\theta_0}, \quad b_2 = 4\pi(1 - k_0), \quad Q_1 = \frac{Q_\theta \tau_0}{\rho_m C_m \Delta\theta_0}, \quad Q_2 = \frac{Q_\sigma \tau_0}{\sigma_0}, \quad \tau_0 = (\beta_*^3 \Delta\theta_0^3 I_0)^{-1/4}, \\ l_0 = \left(\frac{\beta_* \Delta\theta_0}{I_0} \right)^{1/4}, \quad x = s - s_*, \quad x_0 = s_p - s_*, \quad \gamma = \tau_0 h, \quad I_0 = I(\Delta\theta_0), \end{aligned} \quad (6)$$

Substituting the dimensionless parameters (6) into the model equations (1)-(5), we rewrite the governing equations in dimensionless form as

$$\frac{dT}{dt} = Q_1(t) + b_1 w \int_0^{x_0} (x + s_*)^2 \left(F(x, t) - u_0 \frac{\partial F}{\partial x} \right) dx, \quad t > 0, \quad (7)$$

$$\frac{dC}{dt} = Q_2(t) + b_2 w C \int_0^{x_0} (x + s_*)^2 \left(F(x, t) - u_0 \frac{\partial F}{\partial x} \right) dx, \quad t > 0, \quad (8)$$

$$\frac{\partial F}{\partial t} + w \frac{\partial F}{\partial x} + \gamma F = u_0 w \frac{\partial^2 F}{\partial x^2}, \quad t > 0, \quad 0 < x < x_0, \quad (9)$$

where

$$w = T_* - \frac{m\sigma_0}{\Delta\theta_0} C_l - T_l, \quad t > 0, \quad (10)$$

$$w = 1, \quad F = F_0(x), \quad T_l = T_0, \quad C_l = 1, \quad t = 0; \quad F = 0, \quad x = x_0, \quad (11)$$

$$F - u_0 \frac{\partial F}{\partial x} = J(w), \quad x = 0; \quad (12)$$

where $J(w) = \exp(p\varphi(w))/w$ and

$$\varphi(w) = \begin{cases} 1 - w^{-2} \\ \ln w \end{cases}.$$

Here, as above, the first and second lines define the function $\varphi(w)$ for the Weber-Volmer-Frenkel-Zeldovich and Meirs kinetic mechanisms, respectively.

3 | ANALYTICAL SOLUTIONS

Let us solve the equation (9) using the variable separation method. The auxiliary function can be written out as

$$F_1(x, t) = F(x, t) - \frac{J(w(t))(x_0 - x)}{x_0 + u_0}, \quad (13)$$

where $J = 1$ at $t = 0$ (at $w = 1$).

As a result, after mathematical transformations, F_1 takes the form

$$F_1(x, t) = \sum_{k=0}^{\infty} \exp(-\xi_k(t)) X_k(x) \left[F_{0k} + \int_0^t v_k(t_1) \exp(\xi_k(t_1)) dt_1 \right], \quad (14)$$

$$\xi_k(t) = \frac{S_k(t)}{4u_0}, \quad S_k(t) = (1 + 4u_0^2 n_k^2) \int_0^t w(t_1) dt_1 + 4u_0 \gamma t,$$

where $X_k(x)$ are the eigenfunctions

$$X_k(x) = \exp\left(\frac{x}{2u_0}\right) [2n_k u_0 \cos(n_k x) + \sin(n_k x)], \quad (15)$$

and n_k are the eigenvalues

$$2n_k u_0 \cos(n_k x_0) + \sin(n_k x_0) = 0, \quad k = 0, 1, 2, \dots \quad (16)$$

As $S'(t)$ is positive, we can estimate the aforementioned integrals using the saddle-point method as³⁴

$$\int_0^t v_k(t_1) \exp\left(\frac{S_k(t_1)}{4u_0}\right) dt_1 \approx \frac{4u_0 v_k(t) \exp[S_k(t)/(4u_0)]}{S'_k(t)}. \quad (17)$$

Substitution (17) into (16) leads to

$$F_1 \approx \sum_{k=0}^{\infty} X_k(x) \left[F_{0k} \exp(-\xi_k(t)) + \frac{4u_0 v_k(t)}{(1 + 4u_0^2 n_k^2) U'(t) + 4u_0 \gamma} \right], \quad U(t) = \int_0^t w(t_1) dt_1. \quad (18)$$

Now, we can express T_l from (10) and substitute it into (7). The result is

$$-\frac{m\sigma_0}{\Delta\theta_0} \frac{dC}{dt} - \frac{dw}{dt} = Q_1(t) + b_1 w \int_0^{x_0} (x + s_*)^2 \left(F - u_0 \frac{\partial F}{\partial x} \right) \quad (19)$$

To simplify the formulas, let's make the following replacement:

$$I = \int_0^{x_0} (x + s_*)^2 \left(F - u_0 \frac{\partial F}{\partial x} \right), \quad M = \frac{m\sigma_0}{\Delta\theta_0}. \quad (20)$$

From (19), we express dC/dt as

$$\frac{dC}{dt} = -\frac{1}{M} (Q_1 + U'' + b_1 U' I). \quad (21)$$

From (8), we express C as

$$C = -\frac{Q_1 + U'' + b_1 U' I + Q_2 M}{M b_2 w I}. \quad (22)$$

Differentiating the last formula and combining it with (21), we arrive at the expression

$$(Q_1' + U''' + b_1 U'' I + b_1 U' I' + M Q_2') U' I + (Q_1 + U'' + b_1 U' I + Q_2 M)(U'' I + U' I') \quad (23)$$

$$= (Q_1 + U'' + b_1 U' I) b_2 U'^2 I^2. \quad (24)$$

Finally, combining (18) and (24), we come to the following Cauchy problem

$$U''' = P(U'', U', U, t), \quad U'' = U_{sd}, \quad U' = 1, \quad U = 0, \quad t = 0, \quad (25)$$

where the functions P and U_{sd} are determined in the Appendix.

4 | CONCLUSION

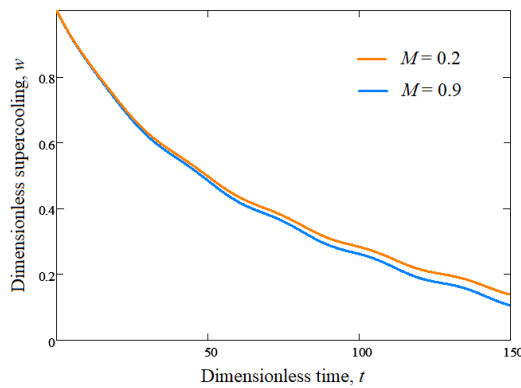


FIGURE 1 The dimensionless supercooling versus the dimensionless time t .

Let us summarize in conclusion the main outcomes following from our analysis. So, the mathematical model under consideration describes a metastable binary system in a crystallizer, where the solid phase particles nucleate and evolve. Using the saddle-point method for calculating the Laplace-type integral, an analytical solution is constructed. This solution determines

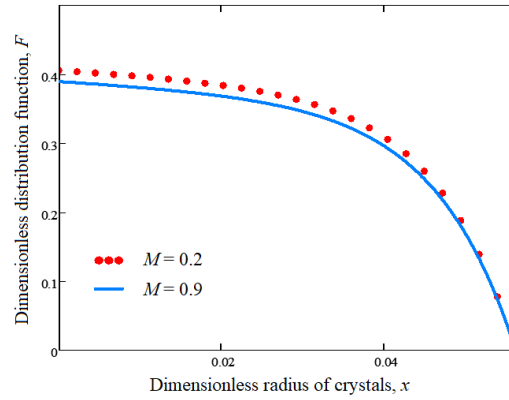


FIGURE 2 The dimensionless distribution function versus the dimensionless radius x .

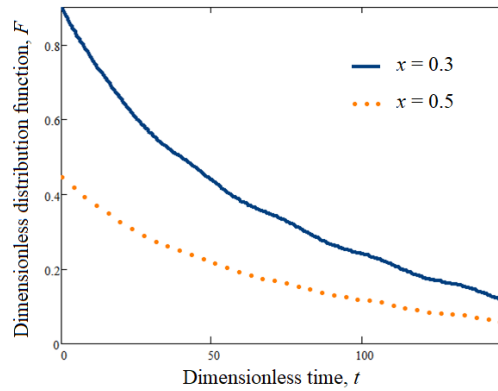


FIGURE 3 The dimensionless distribution function versus the dimensionless time t .

the dynamic dependencies for the melt supercooling and the crystal-size distribution function. The theory presented can be applied to any nucleation kinetics. As special cases, two important mechanisms of the Weber-Volmer-Frenkel-Zel'dovich and Meirs kinetics are considered. Figure 1 demonstrates how dimensionless supercooling changes with time. Here the desupercooling behavior is presented for different values of the system parameter M that determines the impurity concentration of a binary melt. It is easy to see that supercooling is removed faster with an increase in the impurity concentration of a binary melt. This is explained by the fact that the more impurities in the supercooled system, the more intensively the nucleation of a new phase occurs on impurity particles. In Figure 2, we can see that there are more crystals with a smaller radius than crystals with a larger radius in a supercooled melt. In addition, larger impurity concentrations (larger values of the parameter M) lead to smaller particle-radius distribution function. Also note, that this function vanishes at a certain value of x as the product crystals are removed from the crystallizer (at $x = x_0$). Figure 3 shows the dimensionless distribution function versus the dimensionless time. It is easy to see that the distribution function plotted for a fixed particle size x becomes smaller over time because the crystals grow and leave the metastable liquid of a crystallizer when their radius becomes equal to the radius of product crystals.

In conclusion, we especially note that the theory of nucleation and growth of crystals in a supercooled binary melt considered in this article can be combined with the theory of directional crystallization in the presence of a two-phase zone using the mathematical theories of directional solidification developed earlier.^{35–43}

APPENDIX

$$\begin{aligned}
 P(U'', U', U, t) &= \frac{R_1 b_2 U'^2 I^2 - R_2 U' I + R_3 (U'' I + U' B)}{(1 + b_1 U' A) U' I + R_3 U' A}, \\
 R_1 &= Q_1 + U'' + b_1 U' I, \quad R_2 = Q'_1 + b_1 U'' I + b_1 U' B + M Q'_2, \quad R_3 = Q_1 + b_1 U' I + U'' + M Q_2, \\
 U_{sd} &= -M Q_2(0) - Q_1(0) - (b_1 + M b_2) I, \\
 A &= - \sum_{k=0}^{\infty} (Z_k - u_0 Y_k) \frac{\nu_{k3} J 4 u_0}{s'_k U'}, \\
 B &= \sum_{k=0}^{\infty} (Z_k - u_0 Y_k) \left[F_{0k} \exp\left(\frac{-s_k}{4u_0}\right) \left(\frac{-s'_k}{4u_0}\right) \frac{4u_0 E s'_k - 4u_0 \nu_k s''_k}{(s'_k)^2} \right] + \frac{u_0 \sigma J'}{x_0 + u_0} + J' \Psi, \\
 E &= \nu_{k1} (JU)' - \nu_{k2} J' - \nu_{k3} (J'' - KU'''), \quad K = -\frac{\exp(p\varphi)}{(U')^2}, \\
 I &= \sum_{k=0}^{\infty} (Z_k - u_0 Y_k) \left[F_{0k} \exp\left(\frac{-s_k}{4u_0}\right) + \frac{4u_0 \nu_k}{s'_k} \right] + J \Psi + \frac{u_0 \sigma J}{x_0 + u_0}, \\
 \Psi &= \frac{(x_0 + s_*)^4 - 4s_*^3(x_0 + s_*) + 3s_*^4}{12(x_0 + u_0)}, \quad \delta = \frac{(x_0 + s_*)^3}{3} - \frac{s_*^3}{3}, \\
 Z_k &= \int_0^{x_0} (x + s_*)^2 X_k(x) dx, \quad Y_k = \int_0^{x_0} (x + s_*)^2 \frac{dX_k(x)}{dx} dx, \\
 s_k &= (1 + 4u_0^2 n_k^2) U' + 4u_0 \gamma, \quad \nu_{k1} = \frac{1}{I_k(x_0 + u_0)} \int_0^{x_0} X_k(x) \exp\left(\frac{-x}{u_0}\right) dx, \\
 \nu_{k2} &= \frac{\gamma}{I_k(x_0 + u_0)} \int_0^{x_0} (x_0 - x) X_k(x) \exp\left(\frac{-x}{u_0}\right) dx, \quad \nu_{k3} = \frac{(p-1)\nu_{k2}}{\gamma}.
 \end{aligned}$$

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Author contributions

The authors contributed equally to the present research article.

Conflict of interest

The authors declare no potential conflict of interests.

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