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Nucleation and crystal growth kinetics during solidification: The role of crystallite withdrawal rate and external heat and mass sources

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HIGHLIGHTS

- The article deals with a problem of transient nucleation at the intermediate stage of phase transitions in crystallizers.
- A new analytical method based on the saddle-point technique is developed.
- The Fokker–Planck and balance equations are solved in the presence of crystallite withdrawal rate and external sources.
- An exact analytical solution is constructed for arbitrary nucleation mechanisms and growth kinetics.
- The Weber–Volmer–Frenkel–Zel'dovich and Meirs kinetics are considered in some detail.

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ABSTRACT

A complete analytical solution of the integro-differential model describing the transient nucleation and growth of the crystals at the intermediate stage of phase transitions is constructed. The roles of external heat/mass sources appearing in the balance equations and the crystallite withdrawal rate entering in the Fokker–Planck equation are detailed. An exact analytical solution of the Fokker–Planck equation is found for arbitrary nucleation mechanisms and growth kinetics. Two important cases of the Weber–Volmer–Frenkel–Zel'dovich and Meirs kinetics are considered in some detail. A non-linear time-dependent integral equation with memory kernel for the metastability level is analytically solved on the basis of the saddle-point method for the Laplace integral in the case of mixed kinetic-diffusion regime of crystal growth, which is of frequent occurrence. It is shown that the desupercooling/desupersaturation rate decreases with increasing the crystal withdrawal rate and intensities of external sources. The density distribution function becomes more and more broad with time. In addition, this function increases with decreasing the crystallite withdrawal rate and with increasing intensities of external sources.

1. Introduction

Industrial production of many kinds of materials from supercooled melts and supersaturated solutions is very important for many metallurgical, chemical and pharmaceutical products (Mullin, 1972; Barrett et al., 2005; Larsen et al., 2006; Abu Bakar et al., 2009; Kelton and Greer, 2010). The final goal of every industrial crystallization process is to obtain crystals of a given size, shape, composition, and internal structure. This goal is achieved using a variety of methods based on the main mechanisms: nucleation of crystals and their subsequent growth. The formation and evolution of nuclei in batch crystallizers is essentially a dynamic process controlled by the competition among the crystal withdrawal rate, the intensity of external heat (mass) sources and the rate of metastability reduction, which is dependent on both the nucleation frequency and growth rate of crystals. A deeper understanding of these processes is of great importance in relation to the nucleation and crystal growth phenomena as well as to the design, operation and control of industrial crystallizers. The governing equations of this process represent highly nonlinear system of integro-differential equations. This explains why mathematical methods to study the dynamic behavior of such complicated systems are poorly elaborated.

From the theoretical point of view it is convenient to distinguish four main process stages (Buyevich and Ivanov, 1993; Barlow et al., 2004; Shneidman, 2011). First, there is the preliminary stage, during which a supercooled/supersaturated state develops. In the second stage, critical nuclei of the new phase appear and evolve under the constant metastability (supercooling/supersaturation). These nuclei can be formed heterogeneously around ions or dust particles or homogeneously in the interior of a metastable system. In the third intermediate stage, nucleation of crystals, their growth

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and metastability reduction (desupercooling/desupersaturation) occur. The fourth relaxation stage describes the Ostwald ripening and agglomeration processes. An important distinguishing feature of the phase transition process in a crystallizer is the dependence of the mass (heat) balance equation on intensity of external mass source (heat sink) as well as the dependence of the Fokker–Planck kinetic equation on the crystal withdrawal rate. An attempt of allowing simultaneously for the aforementioned mechanisms in batch crystallizers has been made previously by Buyevich et al. (1991) (see also the similar theory developed by Buyevich and Natalukha (1994) for the combined polymerization and crystallization in continuous apparatuses). However, the governing integro-differential equations describing the nucleation and growth processes in a batch crystallizer have been integrated only for the asymptotic regime of large crystallization time τ. In addition, the final analytical solution has been presented as a non-linear functional integro-differential equation for the relative supercooling/supersaturation even in the limiting case $\tau \to \infty$ analyzed by Buyevich et al. (1991).

The main task of the present study is to develop a new theoretical approach for the construction of analytical solutions of the integro-differential model, describing the nucleation of crystals and their subsequent growth at the intermediate stage of phase transitions complicated by the crystal withdrawal rate and external mass/heat sources/sinks in a crystallizer.

2. Nucleation and crystal growth

In this paper, the previously developed model (Alexandrov and Malygin, 2013, 2014; Alexandrov and Nizovtseva, 2014) of bulk crystallization from a supercooled melt or supersaturated solution is extended to processes which, in addition to nucleation and growth of crystals of the new phase, include the mass (heat) exchange with the surroundings and removal of the crystallites from the mother metastable medium. The supercooling/supersaturation in the system is regarded as macroscopically homogeneous throughout the tank volume considered (homogeneity is achieved in practice by intensive mixing of the system). Physical properties of both the melt/solution and the solid phase are assumed to be constant and independent of supercooling/supersaturation, time and spatial coordinates. The resulting crystals are removed from the system and the total volume of the new phase nuclei is much smaller than the volume of the liquid phase. Under these conditions the evolution of each crystal is independent of the behavior of the remaining solid phase nuclei. It is also assumed that the system supercooling/supersaturation is such to prevent any noticeable agglomeration or breaking of solid crystals. An important point is that variations of crystal habit are negligible, and therefore we define the nucleus size with the help of a single parameter – the radius of a spherical crystallite.

Crystallization from a supercooled melt is described by the heat balance equation written for the system temperature θ

$$\rho_m C_m \frac{d\theta}{d\tau} = Q_1 + 4\pi\rho_s L \int_{r_*}^{\infty} f(\tau,r) r^2 \frac{dr}{d\tau}\, dr, \quad \tau>0, \ r>r_*, \tag{1}$$

where ρ_m and C_m are the density and specific heat of the mixture, τ is the crystallization time, $Q_1<0$ is the temperature (supercooling) dependent heat flux to the surroundings, ρ_s is the density of the solid phase, L is the latent heat of phase transition, f is the density of crystal radius distribution function, $dr/d\tau$ is the rate of crystal growth, and r_* is the minimum size of the crystals (radius of critical nuclei).

If crystallization occurs from a supersaturated solution the mass balance equation takes the form of

$$\frac{dC}{d\tau} = Q_2 - 4\pi C_p \int_{r_*}^{\infty} f(\tau,r) r^2 \frac{dr}{d\tau}\, dr, \quad \tau>0, \ r>r_*. \tag{2}$$

Here C is the system concentration, C_p is the concentration at saturation, and Q_2 is the concentration (supersaturation) dependent mass flux of the crystallizing substance to the system per unit volume, entering the crystallizer.

The kinetic equation, which has the meaning of the continuity equation in the space of radii and its boundary condition can be written as (Buyevich et al., 1991)

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

$$\frac{dr}{d\tau} f = I, \quad r=r_*, \ \tau>0, \tag{4}$$

where I is the nucleation frequency dependent on the system supercooling/supersaturation. Eq. (3) virtually represents the Fokker–Planck equation for the evolution of the crystal size density distribution function in a crystallizer. The function $g(r)$ expresses the crystal withdrawal rate. This function is inversely proportional to the mean residence time of crystals of size r. The boundary condition (4) determines the flux of nuclei that have overcome the critical barrier.

The growth rate of crystals in supercooled melts and supersaturated solutions has been analytically found and discussed by Alexandrov and Malygin (2013). Let us represent the final result as

$$\frac{dr}{d\tau} = \frac{\beta_* \Delta\theta}{1+\beta_* q r}, \quad \Delta\theta = \theta_p - \theta, \ q = \frac{\rho_s L}{\lambda_l} \tag{5}$$

in the case of supercooled melts and

$$\frac{dr}{d\tau} = \frac{\beta_* \Delta C}{1+\beta_* q r}, \quad \Delta C = C - C_p, \ q = \frac{C_p}{D} \tag{6}$$

in the case of supersaturated solutions. Here β_* is the kinetic parameter, θ_p is the phase transition temperature, λ_l is the temperature conductivity coefficient, and D is the diffusion coefficient. Expressions (5) and (6) include two limiting regimes of crystal growth: the kinetic regime for small crystallites, $\beta_* q r \ll 1$, and the diffusion regime for large crystallites, $\beta_* q r \gg 1$, (Buyevich and Mansurov, 1990).

The nucleation frequency I can be expressed as an exponential function of the energy barrier height (Alexandrov and Malygin, 2013; Buyevich and Mansurov, 1990; Zettlemoyer, 1969; Lifshitz and Pitaevskii, 1981)

$$I(\Delta\theta) = I_* \exp\left(-\frac{p\Delta\theta_0^2}{\Delta\theta^2}\right), \quad p = \frac{16\pi\gamma_i^3\theta_p}{3\rho_s^2 L^2 \Delta\theta_0^2 k_B} \tag{7}$$

if the system is a supercooled melt and

$$I(\Delta C) = I_* \exp\left(-\frac{p}{\ln^2(C/C_p)}\right), \quad p = \frac{16\pi\gamma_i^3 M_s^2}{3\rho_s^2 R_g^2 \theta_s^3 k_B} \tag{8}$$

if the system is a supersaturated solution. Here γ_i is the surface tension, $\Delta\theta_0$ is the initial supercooling, k_B is the Boltzmann constant, M_s is the molecular weight, R_g is the universal gas constant, θ_s is the temperature of solution, and p has the meaning of the dimensionless Gibbs number. Expressions (7) and (8) are called the Weber–Volmer–Frenkel–Zel'dovich nucleation kinetics.

Let us also write down some empirical formulas for I which are frequently used in analyzing many industrial processes for supercooled melts

$$I(\Delta\theta) = I_* (\Delta\theta)^p \tag{9}$$