

SELF-OSCILLATIONS IN PROCESSES OF VOLUMETRIC CRYSTALLIZATION IN
 NONKINETIC REGIMES OF CRYSTAL GROWTH WITH CONSIDERATION FOR
 FLUCTUATIONS OF THE GROWTH RATE

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Periodic processes of the formation of a new phase are investigated in a meta-stable medium for the case of crystallization from supersaturated solutions when phase inclusions grow with fluctuating rates depending on their sizes.

Basic ideas about self-oscillating regimes of the phase transformation in metastable media under the dominating role of the fluctuating mechanism of a crystallization nucleus are developed in [1-4]. Periodic regimes of volumetric crystal formation and boiling with explosions which arise due to the instability of stationary regimes are governed by a strongly non-linear dependence of the nucleation frequency on the degree of supersaturation, supercooling, or superheating with respect to the boundary of a metastable zone corresponding to the thermodynamic phase equilibrium. The data on oscillations of integral characteristics of the disperse phase are in good agreement with the results of both laboratory [5-7] and industrial experiments [2-3]. It is shown that a significant intensification of the process can be achieved through the realization of the volumetric crystallization in self-oscillating regimes [2-4]. In [8], the theory is extended to cases with fluctuations in the growth of crystals playing a significant role, i.e., when there exists the following relation for the complete rate

$$\frac{dr}{dt} = \Psi(r, t) + \sqrt{2D}\xi.$$

However, in [8] only the easiest kinetic regime is considered when the rate of growth does not depend on the size of a crystal. In the present (for determinateness we consider crystallization from supersaturated solutions) the results of [8] are generalized for nonkinetic mechanisms of crystal growth of the following types:

$$\Psi = \frac{1}{r} \beta \left(\frac{c - c_0}{c_0} \right), \quad (1)$$

$$\Psi = \frac{\beta_0 (c - c_0)}{1 + \alpha r}, \quad (2)$$

representing respectively a diffusive regime [9] and a mechanism of crystal growth limited by successive processes of diffusion and a surface deposition reaction of the first order [10].

In order to describe mass crystallization we use the kinetic equation of the evolution of a polydisperse ensemble of crystals in a suspension with the boundary condition in the form of the equality between the effective flow of crystals of minimal size and the frequency of the nucleus formation J and the equation of mass balance for the crystallizing matter taking account of the continuous supply of the supersaturated solution and the absorption of supersaturation by growing crystals

$$\frac{\partial f}{\partial t} + \frac{\partial}{\partial r} (\Psi f) + \gamma f = \frac{\partial}{\partial r} \left(D \frac{\partial f}{\partial r} \right), \quad D = D_0 \beta \left(\frac{c - c_0}{c_0} \right); \quad (3)$$

$$-D \frac{\partial f}{\partial r} + \Psi f \Big|_{r=r_*} = J \left(\frac{c - c_0}{c_0} \right);$$

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$$\frac{dc}{dt} = Q \left(\frac{c - c_0}{c_0} \right) - \rho \int_{r_*}^{\infty} \frac{d}{dt} \left(\frac{4}{3} \pi r^3 \right) f(t, r) dr. \quad (4)$$

Equations (3) and (4) are written on the assumption that the supersaturation and the function of distribution of crystals with sizes in the volume of the system are homogeneous; this corresponds to the hypothesis on ideal mixing with the physical characteristics being constant. The removal of crystals in Eq. (3) is described with the help of the balance relation according to which the number of crystals leaving unit volume of the mixture per unit of time is assumed to be proportional to their concentration with the constant proportionality coefficient γ .

We introduce new variables (for determinateness we consider regime of crystal growth (1), calculations corresponding to condition (2) are similar):

$$\Theta = \gamma D_0 \int_0^t \frac{\beta}{\beta_s} dt, \quad s = \left(\frac{\gamma}{\beta_s} \right)^{1/2} r, \quad f = \varphi r, \quad u = \frac{c - c_0}{c_0},$$

where $\beta_s = \beta(u_s)$, where u_s is the relative supersaturation corresponding to a stationary process. Then Eq. (3) assumes the form

$$\begin{aligned} \frac{\partial \varphi}{\partial \Theta} + \frac{1}{s} \frac{\partial \varphi}{\partial s} \left(\frac{1}{D_0} - 2 \right) + \frac{\beta_s}{\beta D_0} \varphi &= \frac{\partial^2 \varphi}{\partial s^2}, \\ \left(\frac{1}{D_0} - 1 \right) \varphi - s \frac{\partial \varphi}{\partial s} \Big|_{s=s_*} &= \frac{J}{D_0 \beta}. \end{aligned} \quad (5)$$

Assuming in (5)

$$\varphi(\Theta, s) = \Phi(\Theta, s) \exp \left\{ - \int_0^{\Theta} \frac{\beta_s dz}{D_0 \beta [u(z)]} \right\}, \quad (6)$$

we obtain for the function $\Phi(\Theta, s)$ the following equation (assuming $s_* \approx 0$):

$$\begin{aligned} \frac{\partial \Phi}{\partial \Theta} + \frac{1}{s} \frac{\partial \Phi}{\partial s} \left(\frac{1}{D_0} - 2 \right) &= \frac{\partial^2 \Phi}{\partial s^2}, \\ \left(\frac{1}{D_0} - 1 \right) \Phi - s \frac{\partial \Phi}{\partial s} \Big|_{s=0} &= \frac{J}{D_0 \beta} \exp \left\{ \int_0^{\Theta} \frac{\beta_s dz}{D_0 \beta [u(z)]} \right\}. \end{aligned} \quad (7)$$

Applying to (7) the Laplace transform in the variable Θ and letting $\Phi(0, s) = 0$, which corresponds to the developed asymptotic stage of the process when the effect of the initial conditions ultimately vanishes, we obtain

$$\begin{aligned} \frac{d^2 \Phi_p}{ds^2} + \frac{1}{s} \frac{d\Phi_p}{ds} \left(2 - \frac{1}{D_0} \right) - p \Phi_p &= 0, \\ \left(\frac{1}{D_0} - 1 \right) \Phi_p - s \frac{d\Phi_p}{ds} \Big|_{s=0} &= \left(\frac{J}{D_0 \beta} \exp \left\{ \int_0^{\Theta} \frac{\beta_s dz}{D_0 \beta [u(z)]} \right\} \right)_p. \end{aligned} \quad (8)$$

The solution of Eq. (8) is

$$\begin{aligned} \Phi_p &= \frac{(s\sqrt{p})^\nu K_\nu(s\sqrt{p})}{\Gamma(\nu+1) 2^\nu} \left(\frac{J}{D_0 \beta} \exp \left\{ \int_0^{\Theta} \frac{\beta_s dz}{D_0 \beta [u(z)]} \right\} \right)_p, \\ \nu &= \frac{1}{2} \left(\frac{1}{D_0} - 1 \right), \end{aligned} \quad (9)$$

where K_ν and Γ are the Macdonald function and the Euler gamma-function respectively. Applying in (9) the inverse Laplace transform in p and taking account of Eq. (6), we obtain

$$\varphi = \frac{s^{2\nu}}{2 \cdot 4^\nu \Gamma(\nu+1) D_0} \int_0^{\Theta} \frac{J [u(\Theta - \tau)]}{\beta [u(\Theta - \tau)] \tau^{\nu+1}} \exp \left\{ - \int_{\Theta - \tau}^{\Theta} \frac{\beta_s dz}{D_0 \beta [u(z)]} - \frac{s^2}{4\tau} \right\} d\tau. \quad (10)$$

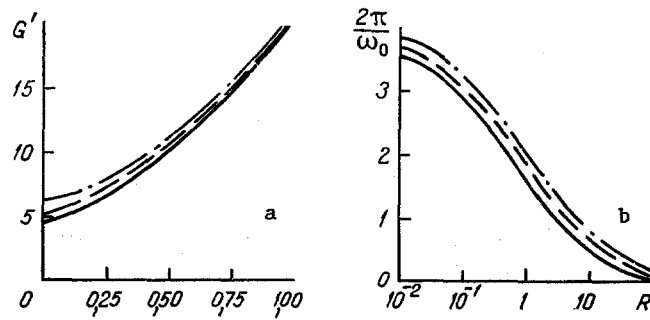


Fig. 1. Characteristics of neutral stability: a) neutral stability curves in the plane of parameters R and G' ; b) oscillation period on the neutral stability curve, $P = 0$, $d = 1$; solid curve, $D_0 = 0$ (result of [4]), dashed line, $D_0 = 0.01$, dashed-dotted curve, $D_0 = 0.05$.

By using (10) in (4) we obtain a functional integrodifferential equation describing the evolution of the relative supersaturation

$$\frac{\beta(u)}{\beta_s} \frac{du}{d\Theta} = \frac{Q(u)}{c_0 \gamma} - \frac{2\pi\alpha\beta}{c_0 \gamma D_0} \left(\frac{\beta_s}{\gamma} \right)^{3/2} \frac{\Gamma(\nu+1,5)}{\Gamma(\nu+1)} \int_0^\Theta \frac{J[u(\Theta-\tau)]}{\beta[u(\Theta-\tau)]} \exp \left\{ - \int_{\Theta-\tau}^\Theta \frac{\beta_s dz}{D_0 \beta[u(z)]} \right\} V \tau d\tau. \quad (11)$$

For $\gamma t \gg 1$ (and this condition is characteristic for many real processes of crystallization in ideal mixing apparatus) with accuracy up to an exponentially small error the upper limit in the integral term in (11) can approach infinity. In this case Eq. (11) admits a stationary solution corresponding to crystallization with the constant nucleation rate

$$Q(u_s) = 2\pi\alpha J(u_s) V \bar{D}_0 \left(\frac{\beta_s}{\gamma} \right)^{3/2} \frac{\Gamma(\nu+1,5)\Gamma(1,5)}{\Gamma(\nu+1)}. \quad (12)$$

The surface of neutral stability of the stationary regime (12) obtained by standard methods of the linear theory of stability is defined by the equation

$$i\omega_0 + Rd - P + (G'_0 - Rd) (1 + i\omega_0 D_0)^{-3/2} + \frac{iRd}{\omega_0 D_0} [(1 + i\omega_0 D_0)^{-3/2} - 1] = 0,$$

in which the following parameters are introduced:

$$R = \frac{Q(u_s)}{c_0 \gamma u_s}, \quad P = Ru_s \frac{d \ln Q}{du} \Big|_{u=u_s}, \quad d = u_s \frac{d \ln \beta}{du} \Big|_{u=u_s}, \quad (13)$$

$$G' = Ru_s \frac{d \ln J}{du} \Big|_{u=u_s}.$$

In Fig. 1a, the trace of the surface of neutral stability $G'_0 = S(R, P, d, D_0)$ is shown in the plane of the parameters G' and R . The condition $G' > S(R, P, d, D_0)$ corresponds to the region of instability. The instability is oscillating in nature (Fig. 1b) and sets in only when the slope of the ascending branch of the function $J(u)$ is sufficiently sharp. With increase in the pulsating component of the crystal growth rate, i.e., with increase in the parameter D_0 , the instability region narrows, and the frequency of oscillations on the surface of neutral stability decreases.

Weakly nonlinear self-oscillating regimes, branching from stationary regimes when passing over the surface of neutral stability to the region of instability, were investigated by methods described in detail in [2, 4]. The results of calculation of the square of the amplitude of the fundamental harmonic and the frequency of self-oscillations with respect to supersaturation

$$q = \frac{G' - G'_0}{G'_0} Z_1(R, P, d, D_0); \quad \omega - \omega_0 = \frac{G' - G'_0}{G'_0} Z_2(R, P, d, D_0)$$

for the power-type kinetics of Mayer nucleation $J = Cu^n$ are given in Fig. 2. It is not difficult to see that throughout the whole region of parameters of the system $q > 0$, i.e.,

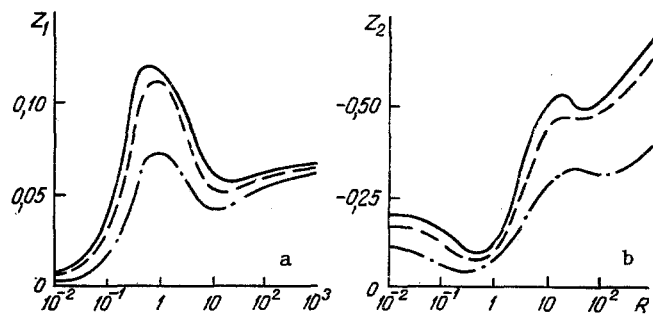


Fig. 2. Dependence of the square of the amplitude of oscillations (a) and frequency shift (b) on the parameter R and supercriticality $G'/G'_0 - 1$ for the power-type kinetics of nucleation $J = Cu^n$, $P = 0$, $d = 1$, solid curve, $D_0 = 0$, dashed, $D_0 = 0.01$, dashed-dotted, $D_0 = 0.05$.

instability is excited weakly. The amplitude of the oscillations increases with penetration into the region of instability, while the frequency decreases. Fluctuations of the rate of growth of crystals result in decreasing the amplitude and increasing the frequency of self-oscillations.

NOTATION

C , n , constants of the power-type Mayer nucleation kinetics; c , concentration of the dissolved matter; c_0 , concentration at thermodynamic equilibrium; D , coefficient of pulsations in the crystal growth rate; D_0 , kinetic coefficient introduced in (3); d , parameter introduced in (13); $f(t, r)$, crystal size distribution function; G' , parameter in (13); G'_0 , magnitude of G' on the neutral stability surface; J , nucleation frequency; K , Macdonald function; P , parameter introduced in (13); p , Laplace transform variable; Q , mass flow; R , parameter introduced in (13); r, r^* , crystal radius and critical crystal radius; s , dimensionless crystal radius; t , time; u , dimensionless supersaturation; α , kinetic coefficient introduced in (2); β, β_0 , kinetic function and the coefficient introduced in (1), (2); γ , rate of removal of crystals from system; Γ , Euler gamma-function; θ , dimensionless time; ϑ , parameter introduced in (9); ξ , Gaussian white noise of unit power, ρ , crystal density; Φ , function introduced in (6); Ψ , averaged crystal growth rate; ω, ω_0 , oscillation frequency and its value on the neutral stability surface; index s refers to quantities corresponding to the stationary crystallization process.

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