length and thus facilitate the diffusion of the nonvolatile component accumulating at the meniscus. The danger of crystals depositing will be the smaller the lower the initial concentration. One can use (10) to estimate the effects of all these factors.

Crystals can form when C_m rises to C_s; (3) shows that the crystallization condition can be put approximately as $\alpha \leq (D/L) \ln C_s/C_0$, which defines an evaporation rate above which crystals may be formed.

NOTATION

C_0, initial concentration; C_m, concentration near meniscus; p_0 and p_m, vapor partial pressures in the surroundings and above the meniscus; C_s, saturation concentration; L, capillary length; r_0, capillary radius; v, flow speed in capillary; α, volume evaporation rate from unit surface, cm/sec; v_m, molar volume of water; R, gas constant; T, temperature, K; Q, salt flux, g/sec; D, salt diffusion coefficient in solution; D_0, vapor diffusion coefficient in air; t, time; ρ, crystal density.

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EFFECTS OF GROWTH RATE PULSATIONS IN BULK-CRYSTALLIZATION OSCILLATIONS

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Weakly nonlinear periodic bulk crystallization conditions are examined in the presence of growth rate fluctuations.

It has been shown [1] that bulk crystallization in a supersaturated or supercooled liquid can give rise to oscillations if the nucleation frequency has a markedly nonlinear relation to the metastability, where the transition to the oscillatory state occurs as a result of normal Hopf bifurcation in the stationary states. It was assumed [1] that each crystal arising in the bulk grows monotonically without rate fluctuations, which is characteristic of many actual processes. However, recent measurements show that growth rates can fluctuate under certain conditions, which may be due to instability in external conditions, e.g., microscopic inhomogeneity or substances active in adsorption [2], or to various processes at the faces such as microrelief change [3] or alternation in defectiveness associated with Frank—Read sources periodically generating dislocation loops [4, 5]. When the growth-rate fluctuations are major, the crystallization acquires some novel features not explicable from the classical model [6, 7]. For example, instead of a monodisperse composition expected for heterogeneous crystallization on ready-made microcrystals of the same size (where nuclei do not arise by fluctuation), and where the nuclei are involved in growth immediately on introduction and grow without forming additional particles, one often gets a resultant distribution with marked size variation [8], which indicates a spread in growth rates. Under certain conditions, the size curves tend to spread as time passes [2, 3, 9-11]. This is also not explicable from the classical theory. The model has been altered to incorporate rate pulsations around the mean, which has explained [2, 3, 9] the distribution spread and the considerable positive skewness, as well as the deformation towards large sizes.

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Growth-rate fluctuations have marked effects if the ratio of the pulsating and average rates is about 0.05; this is quite often so, particularly under industrial conditions, where various external random perturbations occur [8-10]. It is therefore necessary to extend the results of [1] to situations where the rate can fluctuate in order to extend the applications.

Here we consider crystallization from a supersaturated solution; the size of each crystal is [1] characterized by a single parameter: the radius of the sphere equal in volume to the crystal, which corresponds to conditions under which the habit change during growth is slight. The radius change is described by an equation of motion in size space, where the averaged growth rate w(t) is combined with certain random perturbations, i.e., the total rate is

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

where ξ is Gaussian white noise having unit spectral density, which is a superposition of harmonic oscillations at all frequencies having the same amplitude spread. D is a generalized diffusion coefficient and characterizes the probability that a crystal will pass to an adjacent state on the phase axis. The distribution for the polydisperse ensemble in the suspension then varies in accordance with the Kolmogorov—Fokker—Planck evolution equation:

$$\frac{\partial f}{\partial t} + \frac{\partial}{\partial r}(w(t)f) + \gamma f = \frac{\partial}{\partial r}\left(D\frac{\partial f}{\partial r}\right) \tag{1}$$

with boundary condition

$$-D\frac{\partial f}{\partial r}\bigg|_{r=r_*} + w(t)f|_{r=r_*} = J\left(\frac{c-c_0}{c_0}\right). \tag{2}$$

Here γ is the effective mass-transfer coefficient, which characterizes the crystal removal from the system; the assumption that γ is independent of r corresponds to ideal mixing and equal removal probability for crystals of any size.

We have scanty information on how D varies with the parameters, and there is no agreed view; the usual approaches are the assumption that the pulsation coefficient is directly proportional to the average growth rate:

$$D = D_0 w(t),\ D_0 = \text{const [3, 4, 10, 12]} \tag{3}$$

and the relation

$$D = D_0\alpha^m\left(\frac{c-c_0}{c_0}\right)^k,\quad m,\ k = \text{const [13—15]}. \tag{4}$$

As (3) is physically clearer, it is given preference here; in principle, the analysis below can be extended without difficulty to (4).

Homogeneity is assumed, which corresponds to ideal mixing, and also that the solution having a low volume content of new-phase elements is quasihomogeneous, when the mass-transfer balance equation is written as

$$\frac{dc}{dt} = Q\left(\frac{c-c_0}{c_0}\right) - \rho\int_{r_*}^{\infty} f(t,\ r)\frac{dv}{dt}dr,\ v = \frac{4}{3}\pi r^3. \tag{5}$$

We assume that the crystals grow under kinetic conditions with the average rate, which is independent of radius:

$$w(t) = \beta(c-c_0),\ \beta = \text{const}. \tag{6}$$

Here (6) usually gives a good description of many real situations [2, 3, 9-14], and analysis of (1)-(5) for this case is of independent interest.

We solve (1) and (2) by Fourier transformation and get a relation for f(t, r) (assuming $r_* \approx 0$):

$$f(t,\ r) = \frac{1}{2\sqrt{\pi D_0}}\int_0^t \frac{J[u(t-\tau)]}{\sqrt{V}}\exp\left[-\gamma\tau - \frac{(V-r)^2}{4D_0V}\right]d\tau - \tag{7}$$

$$-\frac{\beta c_0}{4\sqrt{\pi D_0}}\int\limits_0^t \frac{f(t-\tau,\ 0)\,u(t-\tau)}{V^{3/2}}(V-r)\exp\left[-\gamma\tau-\frac{(V-r)^2}{4D_0V}\right]d\tau,$$

where the variables are

$$u=\frac{c-c_0}{c_0},\quad V=\beta c_0\int\limits_{t-\tau}^{t} u(z)\,dz. \tag{8}$$

Then (7) gives (5) the form

$$\begin{aligned}c_0\frac{du}{dt}&=Q(u)-4\pi\rho\beta c_0 u\left\{\int\limits_0^t J[u(t-\tau)]\exp(-\gamma\tau)\times\right.\\&\times\left[\frac{V^2}{2}\left(1+\operatorname{erf}\frac{1}{2}\sqrt{\frac{V}{D_0}}\right)+\sqrt{\frac{VD_0}{\pi}}\,V\exp\left(-\frac{V}{4D_0}\right)+\right.\\&\left.+D_0V\left(1+\operatorname{erf}\frac{1}{2}\sqrt{\frac{V}{D_0}}\right)\right]d\tau+\beta c_0\int\limits_0^t f(t-\tau,\ 0)\,u(t-\tau)\times\\&\left.\times\exp(-\gamma\tau)\left[D_0V\left(1+\operatorname{erf}\frac{1}{2}\sqrt{\frac{V}{D_0}}\right)+2\sqrt{\frac{D_0V}{\pi}}\,D_0\exp\left(-\frac{V}{4D_0}\right)\right]d\tau\right\},\end{aligned} \tag{9}$$

where f(t, 0) is defined by an integral Volterra equation of the second kind, which always has the solution

$$\begin{aligned}f(t,\ 0)&=\frac{1}{2\sqrt{\pi D_0}}\int\limits_0^t\frac{J[u(t-\tau)]}{\sqrt{V}}\exp\left[-\gamma\tau-\frac{V}{4D_0}\right]d\tau-\\&-\frac{\beta c_0}{4\sqrt{\pi D_0}}\int\limits_0^t\frac{f(t-\tau,\ 0)\,u(t-\tau)}{\sqrt{V}}\exp\left[-\gamma\tau-\frac{V}{4D_0}\right]d\tau.\end{aligned} \tag{10}$$

Then a difference from the case examined in [1] is that we have to solve (9) and (10); the following important point should also be noted, namely that moment equations were used in [12, 13], where it was assumed without good cause that f(t, 0) = 0, whereas it is readily seen that (10) does not have zero solutions, which means that the corresponding ordinary differential-equation system must be solved with (10) in the moment method.

We extend the analysis on the assumption that the time scale T satisfies $\gamma T \gg 1$, which is so in most real situations and corresponds to examining the developed asymptotic stage. The stationary solution to (9) and (10) is

$$\begin{aligned}f_s(0)&=J(u_s)\left(D_0M^{-1}\beta c_0u_s\gamma\right)^{-1/2}\left(1+2\sqrt{1+M}\right)^{-1},\\Q(u_s)&=4\pi\rho\left(\beta c_0u_s\right)^2D_0\gamma^{-2}J(u_s)\,\Omega,\end{aligned} \tag{11}$$

where

$$\Omega=1+4M^{-1}+(1+M)^{-5/2}\left(4M^{-1}+11+10M+3M^2\right)+\frac{2(1+M)^{-3/2}}{1+2\sqrt{1+M}}\left(1+\frac{3}{2}M+\frac{M^2}{2}\right), \tag{12}$$

and the dimensionless parameter

$$M=\frac{4D_0\gamma}{\beta c_0u_s} \tag{13}$$

characterizes the relative contributions to the growth rate from the pulstion and average components: (7) and (11) can be used directly to calculate bulk-crystallization characteristics in stationary states.

The real stationary state will be described by (11) if it is stable under small supersaturation perturbations; we put

$$u=u_s(1+\xi_0\exp\lambda\theta)\ \text{and}\ f(\theta,\ 0)=f_s(0)(1+f_0\exp\lambda\theta)$$

in (9) and (10) to get a system of two linearized equations describing the perturbation evolution, which has a nontrivial solution is the characteristic determinant $\Delta(\lambda)$ is zero. The complex equation $\Delta(\lambda) = 0$ for $\lambda = i\omega$ defines the neutral-stability surface and the oscillation frequency there:

$$\begin{aligned}&\left(1+\frac{A_{-1}(\omega^\circ)}{2\sqrt{M}}\right)\left(i\omega^\circ-P_1+R+\frac{3g_1^\circ A_{-3}(0)}{2\Omega\sqrt{M}}+\right.\\&+\frac{2g_1^\circ}{\Omega M(1+i\omega^\circ)}\left[2C_{-1}(\omega^\circ)+\frac{3A_{-3}(\omega^\circ)}{4\sqrt{M}}\right]+\frac{2R}{\Omega}B_{-2}(\omega^\circ)+\\&+\frac{4R}{\Omega M}\left[\frac{A_{-1}(0)+\frac{1}{2}A_{-2}(0)}{\sqrt{M}}+C_{-1}(\omega^\circ)\right]+\frac{g_1^\circ}{\Omega}C_{-1}(\omega^\circ)+\\&+\frac{2R}{\Omega(1+2\sqrt{1+M})}\left[C_{-1}(\omega^\circ)+\frac{1}{\sqrt{M}}\left(A_{-1}(0)-\frac{A_{-1}(\omega^\circ)}{1+i\omega^\circ}\right)+\right.\\&\left.\left.+\frac{\sqrt{M}}{2}A_{-2}(\omega^\circ)+\frac{M}{2}B_{-1}(\omega^\circ)\right]+\frac{R}{\Omega\sqrt{M}}\left[A_{-1}(0)-\frac{A_{-1}(\omega^\circ)}{1+i\omega^\circ}\right]\right)-\\&-\frac{2}{\Omega(1+2\sqrt{1+M})}\left[C_{-1}(\omega^\circ)+\frac{\sqrt{M}}{2}A_{-2}(\omega^\circ)\right]\times\\&\times\left(\frac{1+2\sqrt{1+M}}{2\sqrt{M}}g_1^\circ A_{-1}(\omega^\circ)-\frac{R\sqrt{1+M}}{i\omega^\circ}\left[\frac{B_{-1}(\omega^\circ)}{M}+B_0(\omega^\circ)\right]-\frac{RA_{-1}(\omega^\circ)}{2\sqrt{M}}\right)=0,\\&A_k(x)=(1+M^{-1}+ix)^{k+\frac{1}{2}},\quad B_k(x)=M^{-1/2}[A_k(0)-A_k(x)],\\&C_k(x)=M^{-1/2}\left[\frac{A_k(x)}{1+ix}+\frac{A_{k-1}(x)}{2}\right],\end{aligned}\tag{14}$$

where the parameters are

$$R=\frac{Q(u_s)}{c_0\gamma u_s},\quad P_1=\frac{Q'(u_s)}{c_0(\gamma)},\quad g_1=\frac{RJ'(u_s)u_s}{J(u_s)}.\tag{15}$$

Figure 1 shows the trace of the neutral-stability surface $g_1 = S(R, P_1, M)$ in the g_1, R plane. The unstable region corresponds to $g_1 > S(R, P_1, M)$, so instability in the stationary state can set in only if there is sufficiently sharp supersaturation dependence for the nucleation frequency, while for $g_1 < S(R, P_1, M)$, in spite of the fairly marked metastability (R and g_1 are proportional to $J(u_s)$ and $J'(u_s)u_s$ correspondingly with the same coefficient of proportionality), any fluctuation in the stationary supersaturation decays exponentially. Figure 1 shows that the pulsating component (M > 0) tends to stabilize the process, because rate fluctuations lead to certain discrepancies in the elimination of the supersaturation by the growing crystals, which tend to damp the instability. The oscillation frequency at the neutral-stability surface then decreases (Fig. 2).

We assume that the instability with small supercriticality gives rise to a weakly nonlinear oscillation; the dimensionless supersaturation perturbations and f(θ, 0) are represented as Fourier series

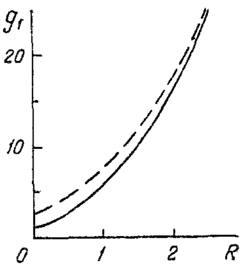

Fig. 1

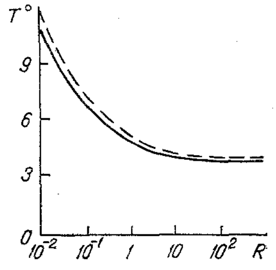

Fig. 2

Fig. 1. Trace of the neutral-stability surface in the g_1, R plane for P_1 = 0; solid line M = 0, dashed line M = 0.1.

Fig. 2. Oscillation period T° = 2π/ω° on the neutral-stability curve; solid line M = 0, dashed line M = 0.1.

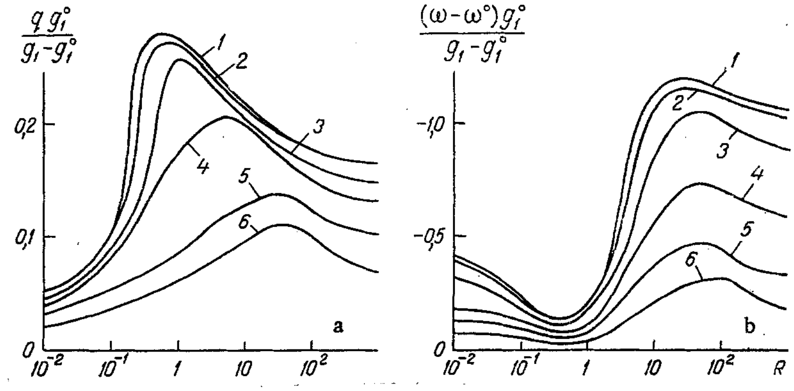

Fig. 3. Weakly nonlinear oscillation characteristics: square of the oscillation amplitude (a) and frequency shift (b) as functions of the parameter R and the supercriticality $g_1/g_1^0 - 1$: 1) M = 0; 2) 0.01; 3) 0.05; 4) 0.1; 5) 1; 6) 10.

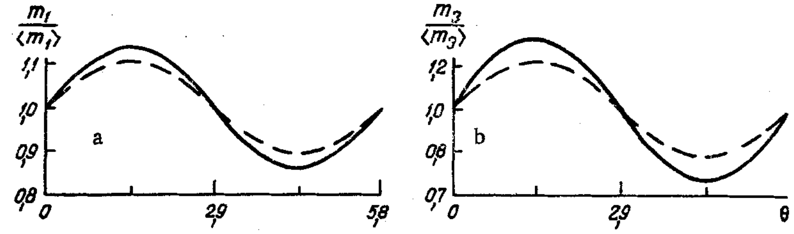

Fig. 4. Effects of growth-rate pulsations on mean size and mean mass yield: solid line M = 0, dashed line M = 0.1, R = 0.5.

$$u = u_s\left[1 + \sum_{n=-\infty}^{\infty} \Phi_n \exp in\omega\theta\right],$$
$$f(\theta,\ 0) = f_s(0)\left[1 + \sum_{n=-\infty}^{\infty} \Psi_n \exp in\omega\theta\right], \tag{16}$$

where $\Phi_n \sim \Psi_n \sim q^{n/2}$, $\Phi_1^2 = \Phi_1\Phi_{-1}$, $\Phi_0 = \Psi \sim q$, $q \sim g_1/g_1^\circ - 1$.

We expand the nonlinear terms in (9) and (10) as series up to the third order of smallness in the perturbations and use (16) to get six equations for the amplitudes Φ_n and Ψ_n having n = 1 and 2 together with Φ_0 and Ψ_0; in the linear approximation, this reduces to two linear equations for Φ_1 and Ψ_1, which define the (14) surface and a linear relation between Φ_1 and Ψ_1:

$$\Psi_1 = \left(\frac{1+2\sqrt{1+M}}{2\sqrt{M}} g_1 A_{-1}(\omega) - \frac{R\sqrt{1+M}}{i\omega}\left[\frac{B_{-1}(\omega)}{M} + B_0(\omega)\right] - R\frac{A_{-1}(\omega)}{2\sqrt{M}}\right)\left(R + \frac{RA_{-1}(\omega)}{2\sqrt{M}}\right)^{-1}\Phi_1. \tag{17}$$

The four equations for the zeroth and second harmonics give Φ_n and Ψ_n for n = 0, 2; one substitutes into the equations for n = 1 to get two linear homogeneous equations for Φ_1 and Ψ_1 (q is to be considered as fixed). We use the linear relation between Φ_1 and Ψ_1 of (17) in the nonlinear terms here; the condition for a nontrivial solution gives a complex equation, which determines the square of the amplitude for the fundamental in the supersaturation perturbation q and the frequency shift $\omega - \omega^0$. These expressions are exceedingly cumbersome and are therefore not given. Figure 3 shows calculations on the amplitude and frequency for the supersaturation oscillations for $J = Cu^n$ nucleation kinetics; positive q correspond to normal Hopf bifurcation in (11) [15, 16] and weakly nonlinear periodic states. The main conclusion in [1] thus persists. As the supercriticality increases, so does the amplitude, while the frequency decreases; when M increases, the amplitude decreases but the frequency increases. Figure 3 shows that the characteristics derived with allowance for the pulsation differ substantially from those in the classical model [1] for M ≈ 0.05, which agrees with the conclusion [2, 3] that rate fluctuations must be considered for such M. Those pulsations also cause a considerable shift in the peak amplitude. Supersaturation oscillations cause oscillations in integral characteristics such as the mean size, surface area, and mass yield (Fig. 4). The mean mass yield on growth with fluctuating rates is unaltered by comparison with that when the fluctuations are negligible.

NOTATION

C and n, constants in the Mayer power-law nucleation kinetics; c, solute concentration; c_0, thermodynamic equilibrium concentration; D, growth rate pulsation coefficient; D_0, kinetic coefficient in (3); f(t, r), size distribution; J, nucleation frequency; m_1 and m_3, moments (first and third orders) of the size distribution; q, square of the amplitude for the fundamental in the saturation perturbation; r, crystal radius; r_*, critical crystal radius; t, time; T, characteristic time scale, u, dimensionless supersaturation; v, crystal volume; w, average growth rate; α, specific mixing rate; β, kinetic coefficient in (6); γ, crystal removal rate from bulk; $\theta = \gamma t$, dimensionless time; ε, gaussian white noise; ρ, crystal density; Φ_n and Ψ_n, amplitudes of harmonic n for the supersaturation perturbations and $f(\theta, 0)$; ω, oscillation frequency. The subscript s denotes that the corresponding quantity relates to the stationary state; ° relates to quantities determined at the neutral-stability surface; an asterisk denotes the complex conjugate; ⟨⟩ time averaging.

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