SOME NONLINEAR EFFECTS OF PHASE TRANSFORMATIONS IN POLYDISPERSE SYSTEMS

I. A. Natalukha

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This article examines quasiperiodic regimes of formation of a new phase in a metastable medium; the effect of different rates of removal of phase inclusions on phase transformation in a polydisperse system is studied.

Processes involving the formation of new phases in a metastable medium – crystallization, boiling, condensation – are usually complicated by a whole range of nonlinear factors which account for the occurrence of different forms of instability and the establishment of oscillatory states. Some of these states were described in [1-4]. The study of unstable phase transformations in heterogeneous media with phase inclusions in the form of crystals, bubbles, and drops is very important both in a scientific sense and for various commercial applications. The problem of the optimum control of nonsteady regimes is especially important [5].

The studies [6-10] examine the basic physical mechanism responsible for loss of stability by steady-state processes and the occurrence of oscillations during phase transformations in the case where a small role is played by active nuclei of the new phase and the major role is played by critical nuclei formed as a result of heterophase fluctuations. The effect of parametric oscillations on the kinetics of formation of the new phase in a metastable medium was investigated in [11, 12]. Here, we attempt to further study parametric resonance and the effect of nonlinearities connected with mass transfer between the system and environment on the dynamic conditions of phase transformations. For the sake of definiteness, below we examine crystallization from supersaturated solutions (the results can be readily generalized to the processes mentioned above).

The mass balance equation for the crystallizing substance is as follows under conditions of intensive mixing of the suspension:

$$\frac{dc}{dt} = Q(c) - (\rho - c)\int_{r_*}^{\infty} \frac{d}{dt}\left(\frac{4}{3}\pi r^3\right) f(t, r)\,dr \tag{1}$$

(a similar equation was written in [6-9] with the assumption that the volume concentration of the new-phase elements in the suspension was small compared to unity). The mass flux Q describes both the entry of supersaturated solution into the system and its exit with removal of the two-phase mixture.

With allowance for fluctuations of the rate of growth of the crystals and the boundary condition for it, we can write the kinetic equation for the crystal-size distribution function in the form

$$\frac{\partial f}{\partial t} + \beta(u)\frac{\partial f}{\partial r} + \gamma(r) f = \frac{\partial}{\partial r}\left(D\frac{\partial f}{\partial r}\right),$$

$$-D\frac{\partial f}{\partial r} + \beta(u) f|_{r=r^*} = J(u), \quad D = D_0\beta(u)$$

(the mean rate of growth of the crystals β and the frequency of nucleation J may be arbitrary functions of the relative supersaturation $u = (c - c_0)/c_0$). In describing the evolution of a polydisperse ensemble of crystals, the authors of [6, 8, 9] did not consider the dependence of the rate of crystal extraction on crystal dimensions in the corresponding

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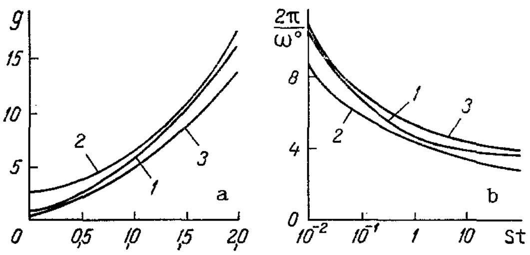

Fig. 1. Characteristics of neutral stability: a) trace of the surface of neutral stability in the plane St, g; b) period of oscillation on the surface of neutral stability for the kinetic regime of crystal growth (R = 1) and Pe = 100: 1) $\gamma = \gamma_0 =$ const; 2) $\gamma=\gamma_0[1-0,1\exp(-10^4 r)]$; 3) $\gamma=\gamma_0[1+0,1\exp(-10^4 r)]$.

kinetic equation. This situation reflects an equal probability of removal of crystals of any size (i.e. γ = const); in [7, 10], the fluctuations of crystal growth rate were assumed to be negligible (i.e. it was assumed that D = 0). Below, we assume that the kinetics of crystal extraction γ is described as below

$$\gamma(r) = \gamma_0[1+\Gamma(r)],\ \Gamma(r) = \Gamma_0\Gamma_*(r),\ |\Gamma_0| \ll 1,\ \Gamma_* \sim 1.$$

It should be noted that this case is frequently encountered in practice and corresponds to small deviations from ideal mixing of the suspension. In this case, the probabilities of the removal of fine and coarse crystals are different (see [3, 13, 14], for example). Then the crystal-size distribution function f(t, r) can be represented by a series in powers of the small quantity Γ_0. We obtain the following expressions for the coefficients of this series:

$$f_0(t,\ r) = \frac{1}{2\sqrt{\pi D_0}}\int_0^t \frac{J[u(t-\Theta)]}{\sqrt{V}}\exp\left\{-\gamma_0\Theta - \frac{(V-r)^2}{4D_0V}\right\}d\Theta -$$

$$-\frac{1}{4\sqrt{\pi D_0}}\int_0^t \frac{f_0(t-\Theta,\ 0)\beta[u(t-\Theta)](V-r)}{V^{3/2}}\exp\left\{-\gamma_0\Theta - \frac{(V-r)^2}{4D_0V}\right\}d\Theta,$$

$$f_m(t,\ r) = -\frac{1}{4\sqrt{\pi D_0}}\int_0^t \frac{f_m(t-\Theta,\ 0)\beta[u(t-\Theta)](V-r)}{V^{3/2}}\times$$

$$\times\exp\left\{-\gamma_0\Theta - \frac{(V-r)^2}{4D_0V}\right\}d\Theta - \frac{\gamma_0}{\pi}\int_0^t\int_0^\infty [\Gamma_*(r)f_{m-1}(t-\Theta,\ r)]_{r\to p}\times$$

$$\times\exp(-\gamma_0\Theta - D_0p^2V)\cos(pV-pr)\,dp\,d\Theta,\quad m=1,\ 2,\ 3,\ \ldots, \tag{2}$$

where

$$V = \int_{t-\Theta}^{t}\beta[u(z)]\,dz,$$

while p is the Fourier transform variable. The unknown $f_m(t, 0)$ are successively determined by a chain of Volterra equations obtained from (2) with r = 0. Then Eq. (1) reduces to the form

$$c_0\frac{du}{dt} = Q(u) - 4\pi\beta(u)(\rho - c)\left[\int_0^t J[u(t-\Theta)]\exp(-\gamma_0\Theta)\times\right.$$

$$\times\left\{\left(\frac{V^2}{2}+D_0V\right)\left(1+\operatorname{erf}\frac{1}{2}\sqrt{\frac{V}{D_0}}\right)+\sqrt{\frac{VD_0}{\pi}}\,V\exp\left(-\frac{V}{4D_0}\right)\right\}d\Theta +$$

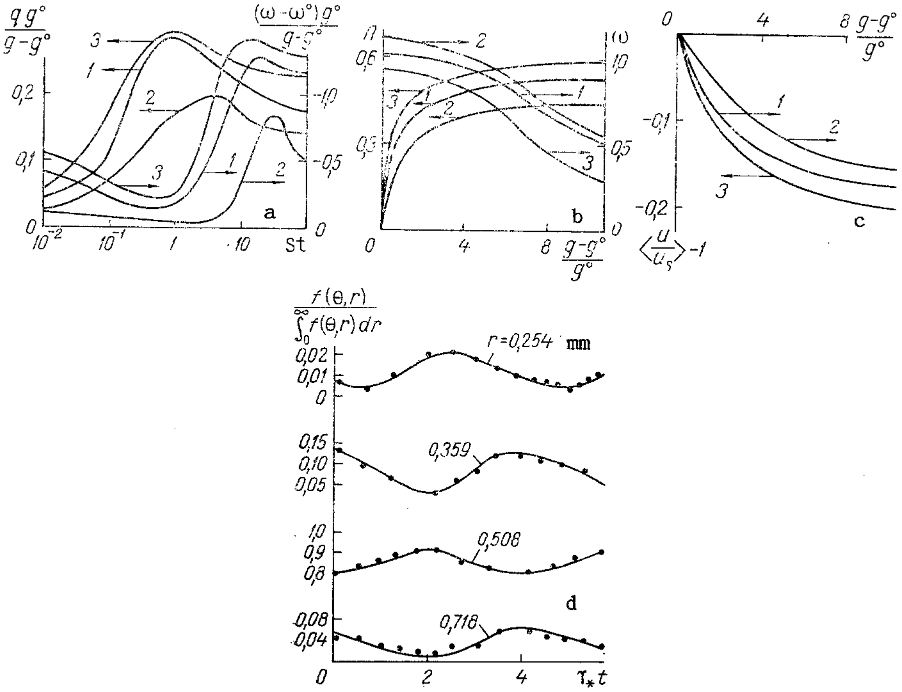

Fig. 2. Characteristics of oscillatory crystallization regimes: a) dependence of the square of the amplitude q of weakly nonlinear oscillations and the frequency shift on the degree of criticality g/g° − 1 at R = 1, Pe = 100; b) amplitude A and frequency ω of strongly nonlinear oscillations of relative supersaturation u/u_s; c) time-averaged degree of metastability $\langle u/u_s\rangle$ at St = 0.5: 1) $\gamma = \gamma_0 = \text{const}$; 2) $\gamma = \gamma_0[1-0{,}1\exp(-10^4 r)]$; 3) $\gamma = \gamma_0[1+0{,}1\exp(-10^4 r)]$); d) comparison of theory (curves) with experiments [13, 14] (points).

$$+\int_0^t\left\{f_0(t-\Theta,\ 0)+\sum_{m=1}^{\infty}\Gamma_0^m f_m(t-\Theta,\ 0)\right\}\beta[u(t-\Theta)]\exp(-\gamma_0\Theta)\times$$

$$\times\left\{D_0V\left(1+\operatorname{erf}\frac{1}{2}\sqrt{\frac{V}{D_0}}\right)+\frac{2D_0^{3/2}}{\sqrt{\pi}}\sqrt{V}\exp\left(-\frac{V}{4D_0}\right)\right\}d\Theta-$$

$$-\frac{\gamma_0}{\pi}\int_0^t\int_0^\infty\int_0^\infty\left[\Gamma_*(r)\sum_{m=0}^{\infty}\Gamma_0^m f_m(t-\Theta,\ r)\right]_{r\to p}\exp(-\gamma_0\Theta-D_0p^2V)\cos(pV-pr)\,dp\,dr\,d\Theta\Bigg] \qquad (3)$$

and together with the above chain of equations for $f_m(t,\ 0)$ determines the evolution of the degree of metastability and the crystal-size distribution function. At $\gamma_0 t \gg 1$, the upper limits of integration in (2-3) and the Volterra equations for $f_m(t,\ 0)$ may approach infinity.

1. Effect of the Dependence of the Rate of Crystal Extraction on Crystal Size on the Neutral Stability of Steady and Amplitude-Dependent Characteristics of Oscillatory Crystallization Regimes. We used linearized analogs of the evolutionary equations to study the neutral stability of steady-state crystallization processes with a constant supersaturation and a definite crystal-size distribution. Figure 1a shows the trace of the surface of neutral stability g = F(St, Pe, R), where

$$\text{St}=\frac{Q(u_s)}{c_0\gamma_0 u_s},\quad g=\text{St}\,u_s\left.\frac{d\ln J}{du}\right|_{u=u_s},\quad R=u_s\left.\frac{d\ln\beta}{du}\right|_{u=u_s},\quad \text{Pe}=\frac{\beta_s}{D_0\gamma_0},$$

in the plane of the parameters St and g for different kinetics of crystal extraction from the system. It is not hard to see that an increase in the rate of extraction of larger crystals stabilizes the system and that the steady-state regime becomes unstable at higher Gibbs numbers than those corresponding to the same extraction rate for crystals of arbitrary dimensions. Such stabilization can evidently be attributed to the fact that it is the

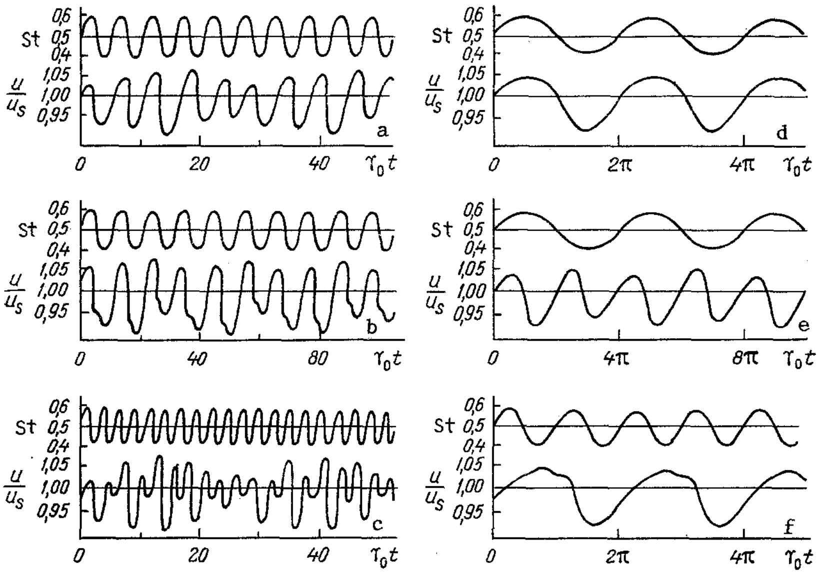

Fig. 3. Characteristics of forced oscillations: a, b, c) quasiperiodic oscillations developing from harmonic, ultra-, and subharmonic oscillations, respectively; d, e, f) oscillations captured by the fundamental, ultra-, and subharmonics (R = 1, Pe = 100, $g/g^\circ - 1 = 0.05$).

coarser crystals that are capable during growth of producing more substantial fluctuations of supersaturation. Their preferential extraction relative to smaller crystals to some extent suppresses the instability caused by these fluctuations. A reduction in the rate of extraction of the coarse crystals has the opposite effect. A higher (compared to fine crystals) rate of extraction of coarse crystals leads to a reduction in the period of oscillations on the surface of neutral stability (Fig. 1b).

The dependence of the kinetics of crystal extraction on crystal size has a significant effect on the characteristics of nonlinear oscillatory crystallization regimes (small-parameter methods similar to those described in [6-8] are used to analyze periodic regimes with a small degree of instability, while numerical methods are used with a large degree of instability, i.e. in the case of developed nonlinearity). Figure 2 shows the results of calculation of the amplitude and frequency of oscillations of supersaturation as functions of the degree of instability and the physical and regime parameters of the system. An increase in the rate of extraction of coarse crystals is accompanied by a decrease in the amplitude of the oscillations (Fig. 2a and b). Here, the time-averaged degree of metastability also decreases (Fig. 2c).

The theoretical results were compared with experimental data from [13, 14] on the crystallization of potassium chloride in the kinetic regime of crystal growth; the characteristic parameters had the following values: St = 0.91; $(g - g^\circ)/g^\circ = 0.09$;

$$\gamma(r) = \begin{cases} 1{,}471\cdot 10^{-4}\ \mathrm{sec}^{-1} & r < 0{,}5\cdot 10^{-4}\,\mathrm{m}, \\ 9{,}748\cdot 10^{-5}\ \mathrm{sec}^{-1} & 0{,}5\cdot 10^{-4}\,\mathrm{m} < r < 3\cdot 10^{-4}\,\mathrm{m}, \\ 1{,}799\cdot 10^{-4}\ \mathrm{sec}^{-1} & r > 3\cdot 10^{-4}\,\mathrm{m}. \end{cases}$$

The frequency of nucleation was described by the Maier formula. Figure 2d shows the satisfactory agreement between the theoretical and experimental findings.

Thus, the kinetics of crystal extraction from the metastable zone, with allowance for the probability of the removal of crystals of different sizes, can be used effectively to stabilize unstable regimes and control oscillatory processes.

2. Quasiperiodic Crystallization Regimes. As was shown in [11, 12], the presence of significant nonlinearities in the system in question makes the use of parametric modulation an effective method of controlling the process. Thus, in a certain interval of modulation characteristics, periodic parametric modulation (modulation of the Stanton number, corresponding to the periodic rate of delivery of the crystallizing substance to the system or the

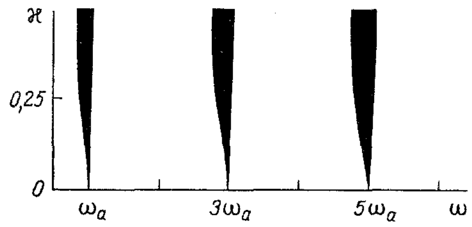

Fig. 4. Regions of capture of the natural frequency with modulation of the parameter St: St = $0.5(1+\varkappa \sin \omega\tau)$, $\tau=\gamma_0 t$, $Q_1=2$, $Q_2=1$, $\mathrm{Pe}=100$, $R=1$, $g/g^\circ-1=0.05$.

rate of removal of elements of the new phase Γ) leads to stabilization of unstable steady-state regimes [11]. In new regions of instability of artificially stabilized regimes, such modulation results in synchronization of the natural frequency of the oscillations with the external frequency. After modulation, the oscillation frequency may coincide with the forcing frequency in a certain frequency range that is sufficiently close to the natural frequency (harmonic capture of the natural frequency by the external frequency). Capture of the natural frequency also occurs when the ratio of the oscillatory and external frequencies are close to an integer different than unity. In this case, the natural frequency is captured by an ultra- or subharmonic [12].

The evolution of the captured oscillations in the transition across the boundary of the frequency synchronization regions was studied numerically on the basis of nonlinear equation (3) for supersaturation in conjunction with a system of equations for the unknowns $f_m(t, 0)$; as in [12], we used the Aitken–Stephensen method. The results obtained show that if the external frequency corresponds to a point located between capture regions, nearly periodic oscillations will develop in the system. In contrast to harmonic, ultraharmonic, and subharmonic oscillations (when the period of the captured oscillations is an integral number of times greater or less than the period of modulation), these oscillations are not strictly periodic, since their amplitude and phase undergo a weakly periodic change (even in the steady-state regime) and the form of the curve is generally not repeated. Also, the ratio of the period of amplitude change and the modulation period in quasiperiodic regimes is expressed by an irrational number. Figure 3a-c shows characteristic cycles of quasiperiodic oscillations that develop from harmonic, ultraharmonic, and subharmonic oscillations with crossing of the boundary of the capture region. The duration of a complete oscillation cycle for the oscillations in Fig. 3a-c is 5.4, 2.9, and 10.4 of the period of parametric modulation, respectively. For comparison, Fig. 3d-f shows the modes of oscillations captured by the fundamental, ultra-, and subharmonic. It is not hard to see that the behavior of the system is qualitatively different in quasiperiodic regimes and the case of frequency synchronization.

3. Suppression of Subharmonic Oscillations by a Nonlinear Source Function.

Synchronization of the frequency of oscillations with an external frequency may be undesirable from a technical standpoint. Under these conditions, the problem of suppressing capture of the natural frequency becomes very important. Analysis shows that an effective means of suppressing synchronization is the introduction of a mass flow which is nonlinear with respect to supersaturation. Thus, under conditions of modulation of the parameter St, a mass flow of the type

$$\frac{Q(u)}{Q(u_s)} = Q_1 - Q_2u^2$$

eliminates capture regions of the order 1/2, 1/4, 1/6,... and leads to a substantial contraction of synchronization regions of the order 1/3, 1/5, 1/7,... (Fig. 4).

NOTATION

c, concentration of dissolved substance; c_0, saturation concentration; D, coefficient expressing the fluctuation of crystal growth rate; D_0, kinetic proportionality factor linking the mean and fluctuation components of crystal growth rate; f(t, r), crystal-size distribution function; $f_m(t, r)$, coefficients of the series expansion of f(t, r); g, product of the Stanton and Gibbs numbers; Pe, fluctuation value of the Peclet number, characterizing the ratio of the mean and fluctuation components of crystal growth rate; p, Fourier transform variable; Q, mass flux; r, r_*, radii of crystal and critical nucleus; t, time; u, dimensionless supersaturation; V, function introduced in (2); St, Stanton number; β, mean rate of crystal growth; $\gamma(r)$, rate of crystal extraction; γ_0, Γ_0, Γ_*, coefficients pertaining to $\gamma(r)$; ρ, density of crystal; ω, frequency of oscillation. The subscript s denotes quantities corresponding to the steady-state regime of crystallization; the superscript ° denotes values on the surface of neutral stability; the index a denotes that a quantity pertains to the natural frequency of oscillation; an asterisk denotes averaging over the ensemble; brackets denote averaging over time.

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OPTICAL AND RADIANT CHARACTERISTICS OF TUNGSTEN AT HIGH TEMPERATURES

S. N. Ivashov and A. I. Fisenko

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It is proposed that thermal radiation spectra of solid materials at high temperatures be treated by the method of moments.

Extensive experimental data have been accumulated on radiant and optical characteristics of solid materials at high temperatures [1-3]. However, the problem of the theoretical treatment of radiant spectra and the related determination of the frequency—temperature dependencies of optical constants is still open today. In the present study, a method is offered that allows one to recreate the radiant spectra from the integral characteristics of the system. The given method has been tested on tungsten. From the generalized Wien displacement law, we determine the temperature for the material under investigation. The calculated values reproduce well the measurement results.

In [4], it is proposed that the absorption spectra be treated by the method of moments. It has been shown that if the experimental outline is a smooth function then it is well reproduced by the asymptotic Edgeworth series. In the present work, a similar method was

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