

A study is made of the instability of nucleation in a metastable medium and a model of significantly nonlinear relaxation self-oscillations which develop when there is an intense dependence of nucleation rate on temperature.

When a liquid is heated rather rapidly, the main mass of vapor-phase nuclei is produced by the fluctuation path, and the role of prepared vapor-formation centers becomes insignificant [1]. As a result, upon rapid and deep entry into the metastable state there is an avalanche-like development of nuclei within the volume of the heated liquid and a rapid growth of bubbles which absorb the superheating heat at an increasing rate. After removal of bubbles from the volume considered, new nuclei appear, and the cycle is repeated. As a result, a unique self-oscillating regime of homogeneous nucleation is established due to competition between heat transfer with the external source and heat loss by growing nuclei.

Similar, but significantly more well-known, phenomena occur in boiling on a wall, where the overwhelming fraction of bubbles is formed on prepared vapor-formation centers, but activation of the latter requires time and significant superheating. Such a situation occurs when the liquid easily wets the solid surface and is especially characteristic of liquid-metal boiling [2, 3]. Explosion-like generation of bubbles on a heating surface depleted of vapor-formation centers lies at the base of the so-called third boiling crisis — a transition to a film regime, which replaces a developed bubble regime [4]. On the whole, as a result of the phenomena described a self-oscillating regime of homo- or heterogeneous boiling can be established, known as "shock," "explosive," or "impulsive" boiling.

An analogous self-oscillating regime is possible with formation of liquid nuclei or solid phase in supercooled vapor or liquid. In this case processes of homogeneous nucleation play a significantly greater specific role than in boiling. Just such a regime may in many cases be responsible for loss of stability of steady-state operating regimes and regular oscillations of the operating characteristics of crystallizers with continuous removal of the crystals formed [5].

Such self-oscillations must lead to periodic oscillations of heater temperatures, heat flux, vapor density in bubbles, concentrations of two-phase systems, etc. The presence in the system considered of natural oscillation frequencies makes possible various resonant phenomena and artificial parametric excitation of oscillations, opening definite possibilities for active interference in the processes of new phase formation in order to intensify heat transfer, increase crystal output, etc. An example of this approach was described in [6].

To the authors' knowledge there is no systematic theory of instability and self-oscillation of this type. Aside from the usual difficulties related to analysis of periodic processes in nonlinear systems, this is apparently related to the lack of adequate physical models for systems with distributed parameters of the type considered, and also to the undeveloped state of the corresponding mathematics. Since the present study is directed toward the principles of the matter, we will consider only the simplest possible, spatially homogeneous model system associated with homogeneous boiling, with a number of simplifying assumption, namely: the liquid's thermophysical parameters and critical nucleus radius  $r_*$  will be considered constant; energy losses to nucleation and the relaxation of the rate of this process to its steady-state value corresponding to a given superheating will be neglected; and the volume concentration of bubbles will be assumed low. Moreover, we will use the simplest possible functions to describe the kinetics of heat supply from without, growth of individual bubbles, and their removal from the system. Generalization of this theory to more complex situations is mainly a matter of more complex mathematics and, as a rule, is obvious.

Evolution Equation. For a dynamic description of the system we will use the heat-balance equation and an equation for the distribution function  $f(t, r)$  of bubbles over radius, normalized to the numerical bubble concentration. The first of these follows from the expression for the elementary quantity of heat obtained by the system corresponding to the first principle of thermodynamics:  $dq = c_x dT + Ldx$ , where  $c_x$  is the heat capacity of the two-phase system for constant mass concentration  $x$  of the elements of the new phase. At a low concentration of the new phase the heat capacity and density of the mixture coincide approximately with the values of  $c$  and  $\rho$  for the liquid. Therefore, the heat-balance equation can be written in the form

$$\rho c \frac{dT}{dt} = \alpha(T_m - T) - \rho_v L \int_{r_*}^{\infty} \frac{dv}{dt} f(t, r) dr, \quad v = \frac{4}{3} \pi r^3. \quad (1)$$

Here  $\alpha$  is the effective coefficient of heat transfer with the external thermostat at temperature  $T_m$  calculated per unit volume of the mixture. The quantity  $T_m$  has the sense of the maximum temperature to which the liquid could be heated if phase transitions were absent. Thus, in Eq. (1) in fact we take  $\rho dq = \alpha(T_m - T)$ ; the assumption of temperature homogeneity in the two-phase mixture corresponds to a system with ideal mixing.

We write the kinetic equation for the distribution function and boundary condition there-to in the form

$$\frac{\partial f}{\partial t} + \frac{\partial}{\partial r} \left( \frac{dr}{dt} f \right) + \gamma f = 0, \quad \left( \frac{dr}{dt} f \right)_{r=r_*} = J \left( \frac{T - T_0}{T_0} \right). \quad (2)$$

Here  $\gamma$  is the effective mass-transfer coefficient;  $J$  is the rate of nucleation, dependent on the relative superheating above the boiling temperature  $T_0$ . In accordance with the hypothesis of ideal mixing the distribution function is also considered homogeneous within the volume occupied by the system, and removal of bubbles is described with the simplest possible balance relationship, according to which the number of bubbles of a given radius leaving a unit volume of the mixture per unit time is proportional to the concentration of such bubbles with a constant proportionality constant  $\gamma$ . In reality, removal of elements of the new phase may occur due to the action of gravity and buoyancy (which is especially characteristic of vapor formation) or as a result of precipitation of such elements on the boundaries of the volume occupied by the mixture (which is characteristic of crystallization). The assumption that  $\gamma$  is independent of  $r$  is a definite idealization, which does not change the essence of the matter, but significantly simplifies calculations. The assumption of system homogeneity presupposes intense mixing, which is obviously difficult to accomplish in boiling liquids, but is quite usual in many types of crystallizers. The boundary condition in Eq. (2) describes behavior in a system of bubbles of minimum size.

We introduce new variables and parameters:

$$u = \frac{T - T_0}{T_0}, \quad u_m = \frac{T_m - T_0}{T_0}, \quad \varphi = \frac{f}{r}, \quad s = r^2, \quad (3)$$

$$\frac{dr}{dt} = \frac{\beta T_0 u}{r}, \quad \beta = \frac{\lambda}{\rho_v L},$$

where  $\lambda$  is the liquid thermal conductivity. The expression used for  $dr/dt$  corresponds to a growth process whose rate is limited by heat supply to the bubble at small Jacobi numbers. This expression is valid for  $r \gg r_*$ ; proof of its suitability is offered by the fact that the main contribution to the integral of Eq. (1) is produced by quite large bubbles. In principle this expression may be regarded as a model one, and if necessary, could be replaced by any other known one (as presented, for example, in [7]).

In the variables of Eq. (3), Eqs. (1) and (2) take on the form

$$\frac{du}{dt} + \left( \frac{\alpha}{\rho c} + 2\pi \frac{\lambda}{\rho c} I \right) u = \frac{\alpha}{\rho c} u_m, \quad I = \int_0^{\infty} \varphi(t, s) \sqrt{s} ds, \quad (4)$$

$$\frac{\partial \varphi}{\partial t} + 2\beta T_0 u \frac{\partial \varphi}{\partial s} + \gamma \varphi = 0, \quad \varphi|_{s=0} = \frac{J(u)}{\beta T_0 u}, \quad (5)$$

where for simplicity in the limits we take  $s = 0$  instead of  $s = r_*^2$ .

System (4), (5) is intensely nonlinear, and our main problem is obtaining a unique equation describing the evolution of the process, i.e., eliminating one of the unknown variables. To do this, we take the Laplace transform of Eq. (5), replacing the variable  $s$  by  $p$ , and obtain

$$\frac{d\varphi_p}{dt} + (2\beta T_0 u_0 p + \gamma) \varphi_p = 2J(u)$$

We will limit our study to the situation at sufficiently large  $t$ , in which case we can, first, neglect the term with the arbitrary constant which appears in the standard form of the general solution of this equation (this implies elimination of the effect of initial conditions) and, second, replace the integral of  $u$  over  $dt$  from zero to  $t$  by  $u_0 t$ , where  $u_0$  is the mean over time of  $u(t)$ , which is approximately valid for  $\gamma t \gg 1$ . We then have

$$\varphi_p = 2 \int_0^t J[u(\tau)] \exp[-(2\beta T_0 u_0 p + \gamma)(t - \tau)] d\tau.$$

Further, with the aid of a new Laplace transform, we transform from the variable  $t$  to  $p'$ :

$$\varphi_{pp'} = \frac{2J_{p'}}{2\beta T_0 u_0 p + p' + \gamma}.$$

Taking the inverse Laplace transform of  $p$  to  $s$ , we have

$$\varphi_{p'} = \frac{J_{p'}}{\beta T_0 u_0} \exp\left(-\frac{p' + \gamma}{2\beta T_0 u_0} s\right).$$

The Laplace transform of the integral  $I(t)$  from (4) has the form

$$I_{p'} = \int_0^{\infty} \varphi_{p'} \sqrt{s} ds = (2\pi\beta T_0 u_0)^{1/2} (p' + \gamma)^{-3/2} J_{p'},$$

so that

$$I(t) = 2(2\beta T_0 u_0)^{1/2} \int_0^t J[u(t - \tau)] e^{-\gamma\tau} \sqrt{\tau} d\tau.$$

At  $\gamma t \gg 1$ , to the accuracy of an exponentially small error the upper limit in the integral obtained can be extended to infinity. Substituting the expression obtained for  $I(t)$  in Eq. (4), we obtain the following integrodifferential evolution equation for the unique variable — the relative superheating  $u$ :

$$\frac{du}{dt} + 4\pi(2\beta T_0 u_0)^{1/2} \frac{\lambda}{\rho c} u \int_0^{\infty} J[u(t - \tau)] e^{-\gamma\tau} \sqrt{\tau} d\tau = \frac{\alpha}{\rho c} (u_m - u). \quad (6)$$

Steady-State Regime Stability. Equation (6) can be regarded as corresponding to a nonlinear system either with an infinite number of degrees of freedom or with distributed parameters. It admits a steady-state solution  $u(t) = u_s$ , and for determination of  $u_s$  we have the transcendental algebraic equation (taking  $u_0 = u_s$ )

$$\frac{(\beta T_0)^{1/2} \lambda (2\pi u_s)^{3/2}}{\alpha \gamma^{3/2}} J(u_s) = u_m - u_s. \quad (7)$$

We will now study the stability of the regime of Eq. (7) by taking  $u = u_s + x$ , with  $|x(t)| \ll u_s$ . Introducing the new dimensionless variables

$$\tau = \gamma t, \quad \xi = \frac{x}{u_s}, \quad \tau_* = \frac{\rho c \gamma}{\alpha}, \quad U = \frac{u_m}{u_s}, \quad g = \frac{u_s J'(u_s)}{J(u_s)},$$

we obtain from Eqs. (6) and (7) a linear equation for the perturbation

$$\tau_* \frac{d\xi}{d\tau} + U\xi + g(U - 1) \frac{2}{\sqrt{\pi}} \int_0^{\infty} \xi(\tau - z) e^{-z} \sqrt{z} dz = 0. \quad (8)$$

Taking  $\xi = \xi_0 e^{\nu\tau}$ , from Eq. (8) one can easily obtain an algebraic equation for the complex parameter  $\nu$ , which splits into two equations for the real and imaginary components of this parameter. After simple calculations we have

$$\tau_* \nu + U + \frac{g(U - 1)}{(1 + \nu)^{3/2}} = 0. \quad (9)$$

In parametric form the neutral stability curve is described by two real equations which follow from Eq. (9) at  $\nu = i\omega$ , where  $\omega$  is a real quantity. Introducing the variables

$$\varphi = \arctg \omega, \quad R = \frac{\tau_*}{U}, \quad S = g \frac{U-1}{U}, \quad (10)$$

we write these equations in the form

$$S \sin \frac{3\varphi}{2} = R(1 + \operatorname{tg}^2 \varphi)^{3/4} \operatorname{tg} \varphi, \quad S \cos \frac{3\varphi}{2} = -(1 + \operatorname{tg}^2 \varphi)^{3/4}. \quad (11)$$

From Eq. (11) we have the equation  $\tan(3\varphi/2) = -R \tan \varphi$ , which has a root  $\varphi = 0$  and a root  $\varphi = \varphi(R)$ , which decreases monotonically from  $\pi/2$  to  $\pi/3$  with increase in  $R$  from zero to infinity. The first root corresponds to the instability condition  $S < -1$ , which in expanded form can be written as

$$\frac{u_s}{J(u_s)} \frac{dJ}{du} \Big|_{u=u_s} < -\frac{U}{U-1}. \quad (12)$$

The second root gives the instability condition

$$\frac{u_s}{J(u_s)} \frac{dJ}{du} \Big|_{u=u_s} > S_*(R) = (1 + \operatorname{tg}^2 \varphi)^{3/4} \left( -\cos \frac{3\varphi}{2} \right)^{-1}. \quad (13)$$

When inequality (12) is satisfied, stability is disrupted with respect to small perturbations of zero frequency, while when inequality (13) is satisfied, stability is lost with respect to perturbations of frequency  $\omega = \tan \varphi(R) > \sqrt{3}$ .

Thus, instability is possible both for increasing and decreasing dependences of nucleation rate on relative superheating (or in the case of crystallization, on relative supercooling), if the dependence is strong enough. Decreasing dependences are naturally not realistic for boiling, but are of interest in crystallization processes. In fact, for the latter, the Tamman effect is known — the function  $J(u)$  has a maximum, caused by abrupt increase in the viscosity of the melt or decrease in the diffusion coefficient in the solution with increase in supercooling. Examples of such functions for crystallization from melts and solutions can be found in [8].

The dependence of the critical value of the parameter  $S_*$  and the perturbation frequency with respect to which stability is initially lost on the parameter  $R = \tau_*/U$  is shown in Fig. 1.

As a result of steady-state regime instability both a gentle increase in self-oscillation amplitude with increase in supercriticality and an abrupt establishment of significantly nonlinear self-oscillations directly after transition through the neutral stability curve are possible. Preliminary analysis indicates that the former is characteristic of increasing, the latter of decreasing, segments of  $J(u)$ . In the first case, for sufficiently low supercriticality slightly nonlinear almost harmonic self-oscillations are established, which can be studied approximately by maintaining in the integrand of Eq. (6) terms of higher order in  $x$  and considering the difference between  $u_0$  and  $u_s$ , as a result of which in place of Eq. (8) we obtain some nonlinear equation. The theory of such self-oscillations is quite complex and thus will be considered separately. Here we will consider the opposite limiting case of self-oscillations of very high amplitude, which may be described approximately as discontinuous oscillations.

Relaxation Self-Oscillations. If the dependence of nucleation rate on relative superheating or supercooling is very intense, it can be approximated by a step function, equal to  $J$  at  $u > u_*$  and zero at  $u < u_*$ . If the value  $J$  is sufficiently large, then at  $u_m > u_*$  relaxation type self-oscillations will appear in the system, which can be studied in the approximation of discontinuous oscillations. As a simple, although not fully representative, example, we will consider the case where the duration of the stay within the system of all bubbles (or other new phase particles) is identical and equal to  $\tau_l$ : any bubble is removed from the system after passage of a time  $\tau_l$  after appearance of the corresponding nucleus.

In this case the phase portrait of the self-oscillation process is approximately a rectangle ABCD in the plane of the variables  $u$  and  $n$ , where  $n$  is the numerical bubble concentration (Fig. 2). On the segment AB the phase trajectory of the process is controlled by the simple equation

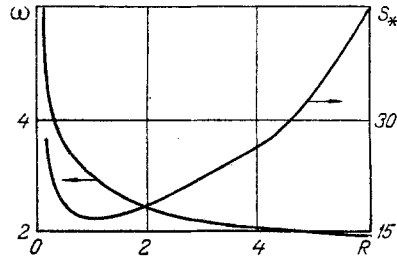


Fig. 1

Fig. 1. Dimensionless frequency and critical value of parameter  $S$  vs parameter  $R$ .

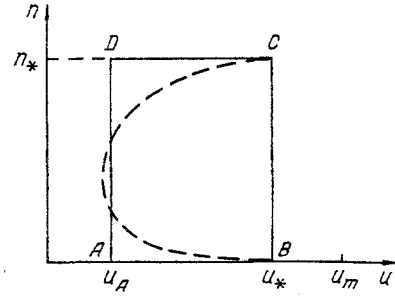


Fig. 2

Fig. 2. Phase portrait of discontinuous self-oscillations.

$$\frac{du}{dt} + \frac{u}{t_*} = \frac{u_m}{t_*}, \quad t_* = \frac{\rho c}{\alpha} = \frac{\tau_*}{\gamma},$$

from which follows

$$u = u_m - (u_m - u_A) \exp\left(-\frac{t}{t_*}\right), \quad t_{AB} = \ln \frac{u_m - u_A}{u_m - u_*}, \quad (14)$$

where  $t_{AB}$  is the time required for displacement of the representative point along this segment from A to B.

At large  $J$  motion from B to C occurs in a jump, completed over a brief time  $t_{BC}$ , over which  $n_*$  nuclei per unit volume are formed in the system. To find this latter value we use the equality of the quantity of heat supplied to the system from without to that absorbed in formation and growth of bubbles in state C, whence we obtain

$$n_* = \frac{\alpha(u_m - u_*)}{4\pi\lambda u_* r_*}, \quad t_{BC} = \frac{n_*}{J} \ll t_{AB} \sim t_*.$$

From this and Eq. (14) it is evident that the condition of "discontinuity" of the self-oscillation is equivalent to the requirement

$$J \gg \frac{\alpha^2}{4\pi\rho c\lambda r_*} \frac{u_m - u_*}{u_*} \ln^{-1} \frac{u_m - u_A}{u_m - u_*}. \quad (15)$$

Assuming that all nuclei are formed practically simultaneously, which is approximately valid when inequality (15) is satisfied, motion of the representative point on the segment CD of the phase trajectory is described by an equation following from Eqs. (1) and (3):

$$\frac{du}{dt} + \frac{u}{t_*} + \frac{4\pi\lambda}{\rho c} n_* \left( r_*^2 + 2\beta T_0 \int_{t_C}^t u(\tau) d\tau \right)^{1/2} u = \frac{u_m}{t_*},$$

which can easily be reduced to a second-order equation if we introduce as the new independent variable the integral of  $u$  over time, and then assume reduction in order upon introduction of  $u$  as the new variable. In the general case the equation obtained must be integrated numerically. However, in real processes over practically the entire time interval ( $t_C, t_D$ ) the inequality  $r \gg r_*$  is satisfied, which obviously corresponds to the inequality  $\Delta t = r_*^2/2\beta T_0 \ll t_*$ . In this case the equation simplifies significantly and its solution can be written in implicit parametric form:

$$u = \left( \frac{dF}{dy} \right)^{-1}, \quad F(y) = -\frac{1}{3u_* z^2} \left[ \ln \frac{(z\sqrt{y} + 1)^2}{z^2 y - z\sqrt{y} + 1} + 2\sqrt{3} \operatorname{arctg} \frac{2 - z\sqrt{y}}{z\sqrt{3y}} \right] \approx t - t_C, \quad z = -\left[ \frac{2}{3} \frac{u_m - u_*}{u_*^2 t_* \sqrt{\Delta t}} \right]^{1/3}. \quad (16)$$

The relative error in Eq. (16) caused by neglect of the initial bubble radius can be significant only over the course of a time of the order of  $\Delta t$  after exit of the system from point C.

The unknown quantity  $u = u_A$  is found by solving Eq. (16) for  $u$  at  $t = t_D$ ,  $t_{CD} = t_D - t_C = t_\tau$ ; at this moment all bubbles practically simultaneously (over the course of a time  $t_{DA} = t_{BC}$ ) leave the system, i.e., the system performs an almost instantaneous jump from state D to state A, after which the process described is repeated.

On the basis of Eq. (14) and the definition of  $t_\tau$  the duration of one full cycle (the self-oscillation period) is equal to

$$t_{AB} + t_{CD} = t_i + t_* \ln \frac{u_m - u_A}{u_m - u_*}, \quad (17)$$

where  $u_A$  is a function of the physical parameters and the time  $t_\tau$ , defined from Eq. (16).

It can easily be seen that for adequacy of the discontinuous relaxation oscillation model used to describe the physical problem only fulfillment of strong inequality (15) regarding nucleation rate is necessary. The supply of heat to the liquid, removal of bubbles, and growth of an individual bubble may be described by relations of quite different types, depending on the concrete conditions of the process. This makes possible effective solution of a very wide class of problems of self-oscillation in boiling, crystallization, etc., on the basis of the general scheme presented above. For example, if there is a distribution of bubbles over duration of stay in the system, then it can be assumed that  $n$  satisfies some independent kinetic equation. Its solution may be used in place of  $n_*$  on the segment of the self-oscillation cycle after the point C, and if practically all bubbles succeed in leaving the system before it attains a superheating  $u_*$ , then the remaining relationships of the procedure are unchanged. The phase trajectory of such a process is depicted by the dashed line of Fig. 2.

#### NOTATION

$c$ , specific heat;  $f$ , distribution function;  $g$ , parameter in Eq. (8);  $I$ , integral in Eq. (4);  $J$ , nucleation rate;  $L$ , latent heat of phase transition;  $n$ , numerical concentration of nuclei;  $r$ , nucleus radius;  $s$ , variable introduced in Eq. (3);  $R, S$ , parameters defined in Eq. (10);  $T$ , temperature;  $T_m, T_o$ , maximum temperature and boiling temperature;  $t$ , time;  $u$ , relative superheating;  $u_m, u_s$ , maximum and steady-state superheat values;  $U = u_m/u_s$ ;  $v$ , volume of nucleus (bubble);  $x$ , superheating perturbation;  $\alpha$ , heat-transfer coefficient;  $\beta$ , coefficient in Eq. (3);  $\gamma$ , mass-transfer coefficient;  $\lambda$ , thermal conductivity;  $\nu$ , complex frequency;  $\xi = x/u_s$ ;  $\rho$ , density;  $\tau$ , dimensionless time;  $\varphi = f/r$ ;  $\omega$ , real frequency; asterisks denote special values of various quantities.

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