

gents are different. This difference is most important for $c^2 = 1$. Therefore, the solutions obtained with and without account of the nonlinearities of the equation of state of the liquid can differ from each other. Thus, Fig. 6 shows the dependence of the soliton amplitude on the square of its velocity ($c_*^2 < c^2 \leq c_e^2$). Curve 1 corresponds to a linear equation of state of the liquid, and curve 2 — to the nonlinear. The equilibrium state of the medium at $\eta_e = \pm \infty$ is of the form $p_e = 2p_0$, $V_e^{-\gamma} = p_e/p_0 = 2$, $k_e = 10^{-4}$, $\dot{V}_e = 0$, $\gamma = 1, 4$, $p_0 = 10^5 \text{ Pa}/\rho_0 c_0^2$. It is seen that for solitons whose velocities squared are smaller than 0.9 the amplitude coincide for the linear and nonlinear equations of state of the liquid. For $c^2 > 0.9$ the amplitudes differ substantially.

Thus, the exact solution of the nonlinear equations of motion of a liquid with gas bubbles has been obtained for one-dimensional stationary perturbations. In this case account of the hydrodynamic nonlinearity and of the compressibility of the liquid component of the medium leads to an extended class of stationary solutions.

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LITERATURE CITED

1. B. S. Kogarko, "One-dimensional, unstable motion of a liquid with generation and development of cavitation," *Dokl. Akad. Nauk SSSR*, **155**, No. 4 (1964).
2. V. V. Goncharov, K. A. Naugo'nykh, and S. A. Rybak, "Stationary perturbations in liquids containing gas bubbles," *Zh. Prikl. Mekh. Tekh. Fiz.*, No. 6 (1976).
3. Yu. Ya. Boguslavskii and S. B. Grigor'ev, "Propagation of arbitrary amplitude waves in a gas-liquid mixture," *Akust. Zh.*, **23**, No. 4 (1977).
4. S. V. Iordanskii, "Equations of motion of a liquid containing gas bubbles," *Zh. Prikl. Mekh. Tekh. Fiz.*, No. 3 (1960).
5. S. V. Iordanskii and A. G. Kulikovskii, "The motion of a liquid containing soft particles," *Izv. Akad. Nauk SSSR, Mekh. Zhidk. Gaza*, No. 4 (1977).
6. R. Cole, *Underwater Explosions* [Russian translation], IL, Moscow (1950).

PROBLEM OF NONSTATIONARY TRANSPORT PHENOMENA IN MULTIPHASE MEDIA

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Nonstationary transport phenomena in multiphase medium in many ways are determined by kinetic processes at the interfaces. The simplest idealizations, introduced during Fourier's and Fick's times, when interphase kinetics were given by the boundary conditions of the type

$$\partial n_i / \partial R = a_{ij}(n_i - n_j),$$

cannot reflect the basic features of transport processes when the physical conditions at the interfaces change considerably and rapidly. This especially concerns problems with mobile boundaries, arising, for example, in analyzing the kinetics of phase transformation [1-5]. In the spherical variant, nonstationary effects arise, in particular, due to Laplacian pressure, which is clearly related to the motion of the boundary ($\sim 1/R(t)$).

We shall give a derivation of the general type of boundary kinetics, based on the process of one-dimensional transport of a fixed component of matter through the interface R of two media (phases), which is the surface of discontinuity for the concentration field of the given component. We shall examine the model indicated schematically in Fig. 1. It assumes that the volume of the media can be separated into some elementary regions of molecular size a_i and, in addition, they can vary in time kinetically and deformationally, i.e., $a_i = a_i(t)$. For solid media, the parameter a_i corresponds to a constant lattice, while for gas media it corresponds to the free path of particles. We assume that the motion of particles occurs in some potential field, whose average relief is shown schematically in Fig. 1. The presence of external and internal fields introduces an asymmetry into the potential relief of the particles, changing the kinetics of their transfer in the forward and backward directions. In what follows, the average velocities of such random wandering W_i will be distinguished

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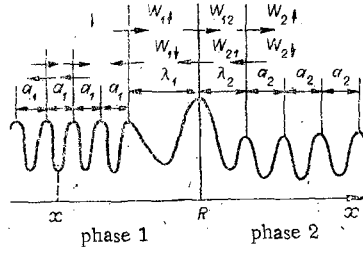


Fig. 1

by orientations of arrows. In addition, we shall assume that the dimensions $\lambda_i(t)$ of the unit cells, directly adjacent to the boundary, are distorted and differ from the bulk cells. The model of the phases proposed combines to some extent the elements of discrete and continuous models.

In accordance with the kinetic scheme in Fig. 1, the conservation laws for the number of particles for two elementary boundary regions, adjacent to the boundary on the left and the right, have the form

$$\begin{aligned} & \frac{\partial}{\partial t} \int_{-\lambda_1(t)}^0 n_1(R+z, t) dz = \frac{1}{\lambda_2} \int_0^{\lambda_2} W_{21}(R+z, t) n_2(R+z, t) dz - \\ & - \frac{1}{\lambda_1} \int_{-\lambda_1}^0 [W_{12}(R+z, t) n_1(R+z, t) + W_{1\downarrow}(R+z, t) n_1(R+z, t)] dz + \frac{1}{a_1} \int_{-a_1}^0 W_{1\uparrow}(R-\lambda_1+z, t) n_1(R-\lambda_1+z, t) dz, \\ & \frac{\partial}{\partial t} \int_0^{\lambda_2(t)} n_2(R+z, t) dz = \frac{1}{\lambda_1} \int_{-\lambda_1}^0 W_{12}(R+z, t) n_1(R+z, t) dz - \\ & - \frac{1}{\lambda_2} \int_0^{\lambda_2} [W_{21}(R+z, t) n_2(R+z, t) + W_{2\uparrow}(R+z, t) n_2(R+z, t)] dz + \frac{1}{a_2} \int_0^{a_2} W_{2\downarrow}(R+\lambda_2+z, t) n_2(R+\lambda_2+z, t) dz, \end{aligned}$$

where n_i are the boundary concentrations of the component examined on the left and right side of the boundary R. The average velocities of wandering $W_{i\uparrow}$, $W_{i\downarrow}$, and the average velocity of crossing through the boundary W_{ij} are calculated by averaging over the corresponding particle distribution functions in a given direction taking into account the transfer probabilities. Expanding and taking into account the transport equation within the volume of the phases, which follow from analogous conservation laws for the elementary regions ($x \pm a_i/2$) and have the form

$$\frac{\partial n_i}{\partial t} = -\frac{\partial J_i}{\partial x} - \delta_i(a_i) n_i, \quad J_i = v_i n_i - \frac{\partial}{\partial x} (D_i n_i), \quad (1)$$

where $v_i = W_{i\uparrow} - W_{i\downarrow}$; $D_i = \frac{a_i}{2} (W_{i\uparrow} + W_{i\downarrow})$; $\delta_i(a_i) = \frac{1}{a_i} \frac{\partial a_i}{\partial t}$, we obtain up to terms linear with respect to the parameters a_i and λ_i that the boundary kinetics are described by the system of equations

$$\begin{aligned} \delta_1 \partial n_1 / \partial t &= u_{11} n_1 + u_{12} n_2 + D_{11} \partial n_1 / \partial R + D_{12} \partial n_2 / \partial R, \\ \delta_2 \partial n_2 / \partial t &= u_{21} n_1 + u_{22} n_2 + D_{21} \partial n_1 / \partial R + D_{22} \partial n_2 / \partial R, \end{aligned} \quad (2)$$

where $\delta_i = \frac{\lambda_i}{2} \left(1 - \frac{2}{3} \frac{\lambda_i}{a_i} - \frac{1}{3} \frac{a_i}{\lambda_i} \right)$;

$$\begin{aligned} u_{11} &= v_1 - \frac{1}{2} \left(1 + \frac{\lambda_1}{a_1} \right) \frac{\partial D_1}{\partial R} - W_{12} + \frac{\lambda_1}{2} \frac{\partial W_{12}}{\partial R} + \frac{1}{3} \left(\frac{\lambda_1^2}{a_1} - \frac{a_1 + 3\lambda_1}{4} \right) \frac{\partial v_1}{\partial R} + \frac{1}{6} \left(a_1 + 3\lambda_1 + 2 \frac{\lambda_1^2}{a_1} \right) \delta(a_1) - \lambda_1 \delta(\lambda_1); \\ u_{22} &= -v_2 + \frac{1}{2} \left(1 + \frac{\lambda_2}{a_2} \right) \frac{\partial D_2}{\partial R} - W_{21} - \frac{\lambda_2}{2} \frac{\partial W_{21}}{\partial R} + \frac{1}{3} \left(\frac{\lambda_2^2}{a_2} - \frac{a_2 + 3\lambda_2}{4} \right) \frac{\partial v_2}{\partial R} + \frac{1}{6} \left(a_2 + 3\lambda_2 + 2 \frac{\lambda_2^2}{a_2} \right) \delta(a_2) - \lambda_2 \delta(\lambda_2); \\ u_{12} &= W_{21} + \frac{\lambda_2}{2} \frac{\partial W_{21}}{\partial R}, \quad u_{21} = W_{12} - \frac{\lambda_1}{2} \frac{\partial W_{12}}{\partial R}; \\ D_{11} &= -\frac{1}{2} \left(1 + \frac{\lambda_1}{a_1} \right) D_1 + \frac{1}{3} \left(\frac{\lambda_1^2}{a_1} - \frac{a_1 + 3\lambda_1}{4} \right) v_1 + \frac{\lambda_1}{2} W_{12}; \\ D_{22} &= \frac{1}{2} \left(1 + \frac{\lambda_2}{a_2} \right) D_2 + \frac{1}{3} \left(\frac{\lambda_2^2}{a_2} - \frac{a_2 + 3\lambda_2}{4} \right) v_2 - \frac{\lambda_2}{2} W_{21}; \\ D_{12} &= \frac{\lambda_2}{2} W_{21}; \quad D_{21} = -\frac{\lambda_1}{2} W_{12}. \end{aligned}$$

The boundary kinetics are sensitive to the structure of the boundary layer. For two variants, when $\lambda_i/a_i = 1/2$ and 1, $\delta_i = 0$ and the boundary conditions are close to the traditional form.

In the spherical case, the boundary conditions on the surface of the sphere are likewise determined by the form (2), but the kinetic coefficients u_{ii} and D_{ii} contain, respectively, the additional terms

$$\frac{1}{3R} \left[\left(a_i + 2 \frac{\lambda_i^2}{a_i} - 3\lambda_i \right) v_i + a_i \left(\frac{\lambda_i^2}{a_i^2} - 1 \right) \frac{\partial D_i}{\partial R} \right], \frac{2a_i}{R} \left(\frac{\lambda_i^2}{a_i^2} - 1 \right) D_i.$$

The boundary kinetics in this case depend explicitly on the coordinates of the interface R. Additional terms will be important only in describing the evolution of micronuclei with dimensions $R \sim \lambda_i^2/a_i$.

Boundary conditions of the type (2) must also occur for nonstationary heat transfer. However, their derivation involves considerable difficulties, stemming from the fact that the transfer of energy occurs along several channels: radiation, collisions, reactions, etc.

Let us consider the case of moveable interfaces, emphasizing processes such as vaporization, dissolution, melting, and the reverse processes. For definiteness, we shall examine a finite two-phase single-component system, closed in the sense that there is no exchange of particles with an external medium. Let us assume that the entire system occupies the interval (0, L) and, in addition, the origin is fixed to phase 1. In this case, the velocity of displacement of the interface is determined by the conservation laws

$$\frac{\partial}{\partial t} \int_0^{R(t)} n_1(x, t) dx = - \frac{\partial}{\partial t} \int_{R(t)}^L n_2(x, t) dx = J_{12}(R, t),$$

where the current through the boundary is given by

$$J_{12}(R, t) = -W_{12}(R, t)n_1(R, t) + W_{21}(R, t)n_2(R, t).$$

Using the volume equations (1), we finally obtain

$$\dot{R} = \gamma_1 + W_{21}Y - D_1X_1 - \frac{J_1(0, t)}{n_1(R, t)} + \sigma_1(a_1) \frac{N_1(R, t)}{n_1(R, t)} = \gamma_2 - W_{12} \frac{1}{Y} - D_2X_2 - \frac{J_2(L, t)}{n_2(R, t)} - \sigma_2(a_2) \frac{N_2(R, t)}{n_2(R, t)}, \quad (3)$$

where

$$X_i = \frac{1}{n_i(R, t)} \frac{\partial n_i}{\partial R}, \quad Y = \frac{n_2(R, t)}{n_1(R, t)}, \quad \gamma_1 = v_1 - W_{12} - \frac{\partial D_1}{\partial R}, \quad \gamma_2 = v_2 + W_{21} - \frac{\partial D_2}{\partial R}, \quad N_1(R, t) = \int_0^{R(t)} n_1(x, t) dx, \quad N_2(R, t) = \int_{R(t)}^L n_2(x, t) dx. \quad (4)$$

The terms $J_1(0, t)$ and $J_2(L, t)$ appear in Eqs. (3) because of the restrictions due to the finiteness and closure of the two-phase system introduced above. It turns out that the finiteness of the system is explicitly manifested in the velocity of the interface. It is as if the separating surfaces feel one another. We also note that the classical variant of Stefan's problem [6], when $\dot{R} = \text{const}$ ($\partial n/\partial R$), is an approximation, which is valid only in exceptional cases.

We shall illustrate the variant when the kinetic parameters do not depend on time explicitly. In this case, there must exist a class of solutions when $n_i(t) = n_i(R(t))$, i.e., the change in concentrations at the interface in time is determined only by the displacement of the interface. From here we have

$$\partial n_i/\partial t = \dot{R} \partial n_i/\partial R. \quad (5)$$

Relations (3)-(5) transform the boundary conditions (2) to the form

$$\dot{R}^2 - \left[\gamma_1 + \frac{D_{11}}{\delta_1} - \frac{I_1}{n_1} + Y \left(\frac{D_1 D_{12}}{D_2 \delta_1} + W_{21} \right) \right] \dot{R} + \frac{1}{\delta_1} \left\{ D_1 \left(u_{11} - \frac{D_{12}}{D_2} W_{12} \right) + D_{11} \left(\gamma_1 - \frac{I_1}{n_1} \right) + Y \left[u_{12} D_1 + W_{21} D_{11} + \frac{D_1 D_{12}}{D_2} \left(\gamma_2 - \frac{I_2}{n_2} \right) \right] \right\} = 0; \quad (6)$$

$$\dot{R}^2 - \left[\gamma_2 + \frac{D_{22}}{\delta_2} - \frac{I_2}{n_2} + \frac{1}{Y} \left(\frac{D_2 D_{21}}{D_1 \delta_2} - W_{12} \right) \right] \dot{R} + \frac{1}{\delta_2} \left\{ D_2 \left(u_{22} + \frac{D_{21}}{D_1} W_{21} \right) + D_{22} \left(\gamma_2 - \frac{I_2}{n_2} \right) + \frac{1}{Y} \left[u_{21} D_2 - W_{12} D_{22} + \frac{D_2 D_{21}}{D_1} \left(\gamma_1 - \frac{I_1}{n_1} \right) \right] \right\} = 0, \quad (7)$$

where

$$I_1 = J_1(0, t) - \sigma_1(a_1)N_1(R, t), \quad I_2 = J_2(L, t) + \sigma_2(a_2)N_2(R, t). \quad (8)$$

The final system of equations (6) and (7) is an algebraic system for the unknowns \dot{R} and $Y = n_2/n_1$, whose quite symmetrical form indicates the simplicity of the qualitative analysis of the system and its approximate solution.

The consistency of the two quadratic equations indicates that one of the roots $\dot{R}_1 = f_1(Y)$ of the first equation (6) necessarily must equal one of the roots $\dot{R}_2 = f_2(Y)$ of the second equation (7). In this case, the condition

$$f_1(Y) = f_2(Y)$$

determines the value of Y in the form of the function

$$Y = n_2/n_1 = \varphi(v_i, W_{ij}, D_i, R, n_i), \quad (9)$$

establishing the relation between the boundary concentrations. The explicit dependence on n_i originates from the terms I_i/n_i in Eqs. (5) and (6) and the explicit dependence on R appears in the case of spherical diffusion, when the kinetic parameters D_{ij} and v_{ij} are functions of R . Substitution of the function φ into the corresponding root of the quadratic equation transforms the law of motion of the boundary into the form

$$\dot{R} = f_1(Y) = f(v_i, W_{ij}, D_i, R, n_i), \quad (10)$$

where the unknown functions $n_i(R)$ still enter. Turning now to Eqs. (3), taking into account the dependences (8)-(10), we obtain

$$\begin{aligned} X_1 &= \frac{1}{n_1} \frac{\partial n_1}{\partial R} = \frac{1}{D_1} \left[\gamma_1 + W_{21} \varphi - f - \frac{I_1}{n_1} \right], \\ X_2 &= \frac{1}{n_2} \frac{\partial n_2}{\partial R} = \frac{1}{D_2} \left[\gamma_2 - \frac{W_{12}}{\varphi} - f - \frac{I_2}{n_2} \right]. \end{aligned} \quad (11)$$

This system determines the boundary concentrations $n_i(v_i, W_{ij}, D_i, R)$, and returning to Eq. (10), the velocity of the boundary and the dependence $R(t)$, i.e., a set of boundary conditions on the moveable boundary is obtained for the solution of the diffusion problem in the bulk of the two-phase medium.

The program presented must essentially be a self-consistent program, since the quantities I_i are functionals of the volume concentrations $n_i(x, t)$. In order to realize the program in practice, it is necessary to postulate from physical considerations the starting values of the quantities I_i .

We shall perform the initial stage of the solution for the particular case of one-dimensional diffusion with constant kinetic coefficients, assuming in the first approximation that $I_i = 0$. As a result of the solution of the system (6) and (7), we obtain

$$Y = n_2/n_1 = \varphi(v_i, W_{ij}, D_i) = \text{const} = n_2(\dot{R}_0)/n_1(R_0) = Y_0, \quad (12)$$

and, in addition, the ratio of the initial concentrations is predetermined by the form of the function φ . Correspondingly, according to (10), we have

$$\dot{R} = f_1(Y_0) = f_0 = \text{const}, \quad R(t) = R_0 + f_0 t. \quad (13)$$

The sign of the quantity f_0 gives the direction of motion. Finally,

$$X_1 = \frac{1}{n_1} \frac{\partial n_1}{\partial R} = \frac{1}{D_1} (\gamma_1 + W_{21} Y_0 - f_0) = \frac{1}{r_*}, \quad n_1 = n_1(R_0) \exp \frac{R - R_0}{r_*}. \quad (14)$$

The subsequent solution of the volume diffusion problem with boundary conditions (12)-(14) gives the form of the functions $I_i(R)$, and the cycle (9)-(11) determines the next approximation. In this case, it is apparently useful to transform the system (11), using relation (9), into the form

$$\begin{aligned} D_1 \partial n_1 / \partial R &= (\gamma_1 - f) n_1 + W_{21} n_2 - I_1, \\ D_2 \partial n_2 / \partial R &= (\gamma_2 - f) n_2 - W_{12} n_1 - I_2, \end{aligned} \quad (15)$$

which after reinstating the dependence $\dot{R} = f(n_1, I_i)$ becomes a determined system. Equations (15) essentially determine the boundary conditions on the moveable interface. We note that for finite and closed systems, they are nonlinear even with constant kinetic parameters v_i, D_i, W_{ij} , when the simplest type of concentration dependence $f = f(I_i/n_i)$ is realized. The specific approximate form of the system of equations (15) can be obtained by substituting into it expansions of the functions f in a series with respect to the corresponding quantities. In addition, one of the equations of the system obtained can be eliminated, if the coupling between n_i is

established from the dependence (9), performing an analogous expansion for the function I_i/n_i , i.e., assuming that $f = f_0 + j_1/n_1 + j_2/n_2$, $1/Y = n_1/n_2 = 1/Y_0 + m_1/n_1 + m_2/n_2$, where

$$j_i = I_i \left(\frac{\partial f}{\partial \frac{I_i}{n_i}} \right)_{I_i=0} ; m_i = I_i \left(\frac{\partial \Phi^{-1}}{\partial \frac{I_i}{n_i}} \right)_{I_i=0} ,$$

we obtain

$$n_2 = \frac{n_1 - m_2}{n_1 + Y_0 m_1} Y_0 n_1, \quad D_1 \frac{\partial n_1}{\partial R} = \left(\gamma_1 - f_0 + Y_0 W_{21} \frac{n_1 - m_2}{n_1 + Y_0 m_1} \right) n_1 - \frac{j_2}{Y_0} \frac{n_1 + Y_0 m_1}{n_1 - m_2} - j_1 - I_1.$$

Subsequent calculations of the boundary concentrations and the law of motion of the boundary $f = \dot{R}$ involve purely technical details.

Investigations of the stability of the motion of the interface, involving determination of the form of the dependence $R = f(R)$, are of great practical interest. This especially concerns the problem of the evolution of spherical nuclei of the new phase.

Stable motion of the interface in a single direction is possible only when the sign of the function $f(R)$ is constant. If, on the other hand, the function $f(R)$ changes sign, then the motion of the boundary is not single-valued. Assume that the change in sign occurs at the points R_i , i.e., $f(R_i) = 0$. Then in the case of $\partial f/\partial R|_{R=R_i} > 0$, a spherical nucleus of the new phase with initial radius $R_0 > R_i$ will grow, while a nucleus with $R_0 < R_i$ will become overgrown. For $\partial f/\partial R|_{R=R_i} < 0$, nuclei with $R_0 < R_i$ grow, while nuclei with $R_0 > R_i$ decrease in size. In the last variant, in the presence of only a single point R_1 , where f changes sign, nuclei of any size in their final development arrive precisely at this size R_1 . The sizes of the nuclei can fluctuate near this equilibrium value.

The existence of zeros of the function $f(R)$ follows from a qualitative analysis of the system of equations (6) and (7). The case $\dot{R} = f(R) = 0$ corresponds to vanishing of the expression in the braces in the system indicated.

We shall limit the analysis to the development of a single spherical nucleus in an infinite medium, when it can be assumed that $I_i = 0$. In deriving the boundary conditions (2), attention was given to the fact that in the spherical variant the kinetic parameters u_{ii} and D_{ii} depend explicitly on the radius and, in addition, $u_{ii} = u_{ii}^{(0)} + c_{ii}/R$, and $D_{ii} = D_{ii}^{(0)} + d_{ii}/R$, where the index 0 relates to coefficients at the plane boundary. For $R = 0$, the structure of Eqs. (6) and (7) assumes the form

$$\begin{aligned} (A_{11} + B_{11}/R)n_1 + (A_{12} + B_{12}/R)n_2 &= 0, \\ (A_{21} + B_{21}/R)n_1 + (A_{22} + B_{22}/R)n_2 &= 0. \end{aligned}$$

This system has nonzero solutions when its determinant, which is determined by the quadratic form relative to $1/R$, vanishes. This indicates the fundamental possibility of the existence of two points R_1 and R_2 , at which $R = 0$. The kinetic scheme of the development of nuclei in this case has two basic variants. If $\partial f/\partial R|_{R=R_1} > 0$, then $\partial f/\partial R|_{R=R_2} < 0$, so that nuclei with $R_0 < R_1$ become overgrown, while the remaining nuclei approach the value R_2 . In the opposite variant, nuclei with $R_0 > R_2$ grow, while the remaining nuclei arrive at a stable state with size R_1 . The situation described is interesting due to the existence of metastable nuclei.

Thus, for the case when the kinetic parameters do not depend explicitly on time and there exists a class of solutions $n_i = n_i(R(t))$, the boundary conditions (2) together with conditions (3)-(5) completely determine the boundary kinetics and the laws of motion of the boundary. The more general case, for which $v_i = v_i(r, t)$, $D_i = D_i(R, t)$, and, correspondingly, $n_i = n_i(R, t)$, requires further analysis.

LITERATURE CITED

1. Ya. I. Frenkel', Statistical Physics [in Russian], Izd. Akad. Nauk SSSR, Moscow (1948); Kinetic Theory of Liquids, Peter Smith.
2. Ya. E. Geguzin, Diffusion Zone [in Russian], Nauka, Moscow (1979).
3. B. Ya. Pines, "Sintering, creep, rest, recrystallization, and other phenomena due to self-diffusion in crystals," Ukr. Fiz. Zh., **52**, No. 4 (1954).
4. I. M. Lifshitz and V. V. Slezov, "Kinetics of diffusion precipitation of oversaturated solid solutions," Zh. Eksp. Teor. Fiz., **35** (1958).
5. V. A. Akulichev, Cavitation in Cryogenic and Boiling Liquids [in Russian], Nauka, Moscow (1978).
6. A. Friedman, Partial Differential Equations, Krieger (1976).