WAVES IN A CHEMICALLY ACTIVE BUBBLED MEDIUM

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We consider numerical models of the wave processes in liquid containing bubbles of a chemically active gas mixture. A number of experimental numerical studies have been carried in this field: from the analysis of the dynamics of single bubbles to two-phase systems. One of the first experimental results was obtained by Soloukhov and Kerdinskii in 1960 when analyzing the behavior of stoichiometric acetylene—oxygen and hydrogen—oxygen mixtures in large, thin-rubber bubbles (about 1 cm in diameter), compressed by a shock wave. The temperature, calculated at the time of ignition from the instantaneous value of the bubble radius on the assumption that its collapse is adiabatic, was compared with the ignition temperature of the mixture. An explosion of the mixture was recorded by a kink in the continuous scan of R(t) (Fig. 1b) in contrast to the case of an inactive mixture (Fig. 1a), by the glow of the explosion products (a similar method was used in [1]), and the state of the bubble after the explosion. In Fig. 1 the bright band across the scan is the result of exposure during an electrically induced explosion of the wire which generates a shock wave.

Hasegawa and Fujiwara [2] noted the possibility of igniting a short chain of vertically arranged bubbles in a shock wave. Detailed experimental studies on the structure of a shock wave in chemically active bubbled media were carried out by Sychev and Pinaev in 1983-87 [3-5]. They found that stationary solitons of the wave-packet type, called bubble-detonation waves, can exist in such media. It turned out that for such solitons to form the amplitude of the initial wave should reach some critical value p_c, which depends essentially on the viscosity of the carrier phase. An increase in p_c does not affect the bubble-detonation wave velocity but does shorten the time in which the system reaches a steady-state regime. It is shown that the propagation velocity D of such a soliton appreciably exceeds the velocity v of the incident wave, which, however, increases if the hydrostatic pressure in the medium is raised. In the last case this wave can overtake and pass the detonation wave [5]: an effect analogous to supercompressed detonation.

Pinaev and Sychev [4] experimentally detected the lower ($K \leq 0.5\%$) and upper ($K \geq 8\%$) limits from the volume concentration K of bubbles in the liquid, when bubble detonation is unstable or disappears. Its propagation increases as K decreases. The amplitudes of the waves in a packet can assume values of 15 to 40 MPa. Pinaev and Sychev [4] point out that, e.g., in experiments with the system H_2O-C_2H_2 + 2.5 O_2 at a bubble diameter of 3-4 mm, bubble concentration $K \approx 6\%$, a zone of ignited bubbles with a length of 6-7 cm, glow time of each such bubble 2-3 μsec, the soliton duration is 100-200 μsec and the soliton velocity (~400 m/sec) increases slightly as the wave propagates. This acceleration is assumed to be due to the gradient of the average density of the medium as a result of hydrostatics.

The above characteristics of the process determine its principal features and serve as control data for checking numerical models. Such models were considered in [6, 7]. In studies on steady-state regimes Shaganov and Vakhitova [6] came to the conclusion that the velocity of a detonation-bubble wave depends weakly on the concentration and the maximum values of its amplitude are $p_{max} \approx 80\ p_0$. As we see, these results differ substantially from the experimental values [3-5]. Elsewhere [7] we analyzed two approaches to the problem: the interaction of an incident shock wave with a single bubble and a two-phase model of the process. The main features of these studies and their development are considered below.

Interaction with a single bubble is an "elementary" act of a complex process of transformation of a wave in a bubbled medium. A detailed analysis, however, revealed a possibly new mechanism of excitation of bubble detonation. An unexpected effect arose upon calculation of the interaction of a strong (50 MPa) plane shock wave with a 2-mm spherical bubble, filled with a 50% mixture of acetylene with oxygen. The intensity of the refraction in shock-wave bubbles was sufficient to initiate detonation in the gas mixture. The reaction began near its wall from the direction of approach of the shock wave long before the collapse

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of the bubble (Fig. 2). Figure 2c shows the profiles of isobars for the time 10.5 μsec; the wave propagates from left to right and a bubble hemisphere is visible in the upper part. In the calculation we used the NOM equation of state for water and detonation products. The activation energy in the Arrhenius equation for the reaction rate is 209 KJ/mole, $z = 6.15 \cdot 10^{27}$ [8]. The results of the calculation graphically demonstrate the effect described above: abrupt jumps in pressure (a) and temperature (b) over the cross section of the bubble.

We can consider experimental results of Hasegawa and Fujiwara [2] as the next step in the development of this field. There an incident shock wave with amplitude ~ 0.7 MPa interacts with a chain of bubbles with diameter ≈ 1 cm, spaced a distance of 5 cm from each other in the direction of the wave propagation. The bubbles are shown to be capable of exploding successively, generating a wave with an oscillating profile, with a velocity much higher than 500 m/sec. The dynamics of a single bubble with a hydrogen—oxygen mixture + 70% Ar was calculated with allowance for the kinetics, described by eleven elementary reactions. Comparison with experiment showed that the calculated degree of compression is substantially lower. Hasegawa and Fujiwara tried to estimate the propagation velocity of the detonation wave, assuming that the incident shock wave is completely absorbed by the first bubble. The explosion of the mixture in it generates a new wave in the liquid, which interacts with the next bubble, etc. The velocity of the wave in a two-phase chain thus is determined by the time of generation of the next wave, i.e., the time of bubble collapse, which corresponds to the time of the explosion of the mixture and the time in which the radiated wave traverses the distance between neighboring bubbles at the speed of sound in the liquid component. This explanation corresponds to the mechanism of wave formation in an inert bubbled system, which was expounded in [9].

The second approach is based on a simplified mathematical model of the two-phase bubbled medium presented in [10]. In the general case it has the form

$$\Delta\zeta = \zeta,\ k_{tt} = -\alpha^2 k^{1/3}\zeta/\rho_0 K_0 + k_t^2/6k, \tag{1}$$

where $\alpha^2 = 3K_0/R_0^2$; $\zeta = p - \delta k^{-\nu}$; $k = (R/R_0)^3$; K_0 and R_0 are the initial volume concentration and the radius of the bubbles; the gas mixture in the bubbles is assumed to behave adiability with adiabatic exponent γ; the average pressure p of the mixture is made dimensionless relative to p_0. Special conditions are adopted when solving system (1) for a chemically active medium. If the temperature reaches the ignition point when a shock-wave bubble is compressed, the mixture explodes instantaneously: the pressure in it and the adiabatic exponent change abruptly with allowance, naturally, for the instantaneous value ρ_* of the gas density at the time of ignition. For example, in the case of stoichiometry γ_* of the acetylene-oxygen mixture of detonation products is assumed to be 1.15 (initial value 1.33) and the pressure and the coefficient δ in the expression for ζ are calculated from the formula $p_* = \rho_*(\gamma_* - 1)\,Q$ (Q is the heat of explosion). This means that for $Q = 2 \cdot 10^6$ J/kg at $y_* = R_*/R_0 \simeq 0.3$ ($T_* = 950$ K) $\delta = 6.47 y_*^{-3\gamma}$ (here $\gamma = 1.33$), i.e., the pressure inside a bubble in products of instantaneous detonation at constant volume is of the order of 80 MPa (calculation from refraction of the wave gives 120 MPa, Fig. 2a).

The problem is formulated as follows. A pressure $p_b(t)$ is given at the boundary of a semi-infinite bubbled medium. The solution should be restricted at infinity. The initial conditions are: $R = R_0$, $k = 1$, and $k_t = 0$ at $t = 0$. A peculiarity of system (1) is that the spatial coordinate x (which is made dimensionless by the factor $\alpha k^{1/6}$) plays the role of a parameter. Calculation showed that as this parameter increases, the time τ_0 necessary for attaining the ignition point of the mixture and the maximum p_{max} of the average pressure in the medium also increase. Thus, at x = 1,2,3, and 4 cm the time τ_0 = 87, 220, 553, and 1386 μsec and p_{max} = 29.5, 37.8, 40.4, and 42.5 MPa, respectively. Indeed, by virtue of the assumption that the liquid component is incompressible, any point of the medium responds instantaneously to a boundary perturbation. Assigning x means assigning the layer thickness $x_0 = x$, in which bubbles collapse synchronously. Initiation of the layer as a whole thus ensues. A nonlinear increase in the energy input corresponds to a linear growth in the volume of the layer in this case: τ_0 increases in a geometrical progression with a coefficient of roughly 2.5 when x changes by 1 cm. The results were obtained for p_b = 3 MPa = const, K_0 = 0.05, and R_0 = 0.2 cm.

We note that given an incompressible liquid component, the effect of the explosion of any layer of the medium on the next parts of it cannot be described with this formulation (an important element of the process, viz., running perturbation, is missing). Without changing model (1), we supplement it with a special condition, which can be defined as a sort of "pump-

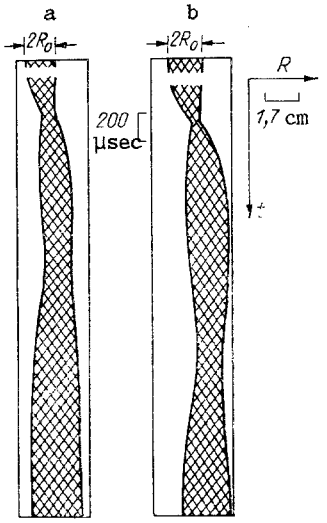

Fig. 1

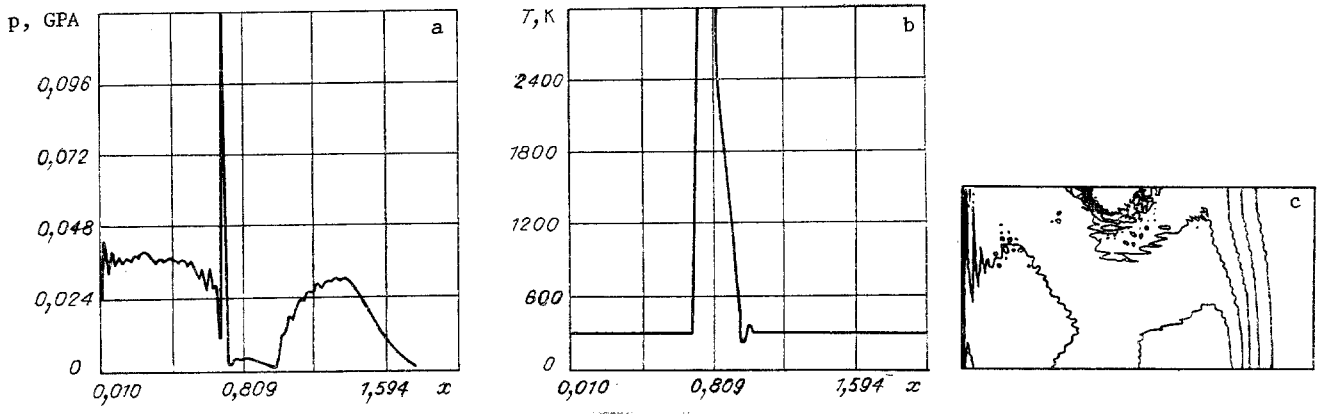

Fig. 2

ing." It is assumed that every time the pressure in the latest exploding bubble becomes a new boundary condition for the remainder of the semi-infinite medium. In the medium that has reacted and is now chemically inactive, the bubbles continue to pulsate under the effect of the initially prescribed pressure at the boundary. This rather artificial approach gave positive results.

A typical picture of the wave field formed is shown in Fig. 3 (for $K_0 = 0.05$ and p_b in the form of a triangle with an amplitude of 2 MPa and a duration of 40 μsec). It gives a sequence of pressure distribution in a bubbled medium, $p_{max} = 0.77$ (1), 0.81 (2), 1.96 (3), and 20.3 MPa (4), for the times (top to bottom) 136, 256, 348, and 400 μsec, respectively. The horizontal scale is $X_0 = 0.6$ cm and the vertical scale is $Y_0 = 2.5$ MPa (5 MPa for 4). The last frame records the time when the detonation wave is formed, attaining a velocity of 300 m/sec and reaches a steady-state regime. Until then the wave in fact propagated with an equilibrium speed of sound of 40-50 m/sec.

Calculations over a wide range of values of K_0 showed that, as in the experiment, the velocity of the bubble detonation wave increases substantially as the concentration decreases: at $K_0 = 0.15$, D = 125 m/sec, and at $K_0 = 0.01$, D = 750 m/sec. The time τ_0 decreases as Pb increases above p_c. A threshold value of K_0 was not found within the framework of the formulation. The oscilloscope trace of the pressure p(t), calculated at a fixed point of the medium, has a characteristic packet structure (Fig. 4a), whose maximum amplitude corresponds to the explosion of the bubble layer with the same coordinate. The series of distinct precursors

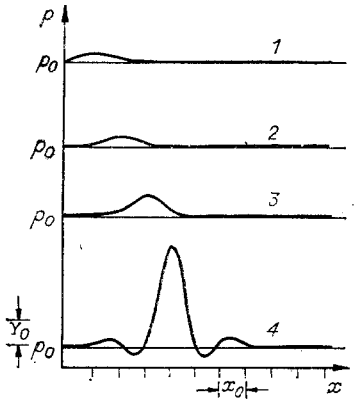

Fig. 3

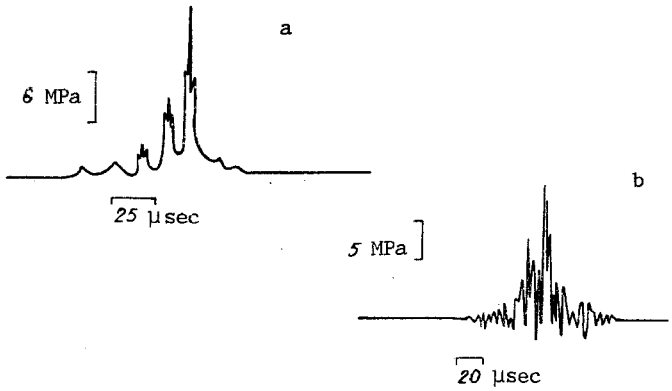

Fig. 4

with growing amplitude are shock waves, from explosions of preceding bubbled layers, that have been transformed during propagation in the layer. Qualitatively the profile of p(t) corresponds to the experimental data (Fig. 4b from [3]), which perhaps indicates a manifestation of the heterogeneity of the physical system used in the experiment. The amplitudes and durations have similar orders of magnitude.

At least two conditions must be taken into account if the possibilities of the two-phase model are to be assessed fully: the kinetics of the chemical reaction in the gas mixture during bubble pulsation and the compressibility of the liquid component of the medium, i.e., the possibility of the transfer of the energy released during the explosion. This energy can compensate for the losses in the incident wave, which decays as it propagates in accordance with the known mechanism of transformation [9, 10] and ensures a self-sustained regime.

We also note that in their experiments [3, 4] Pinaev and Sychev considered more complex structures of the medium, when the carrier phase is the fuel and the bubble contains oxygen. Heat and mass transfer, during which an explosive gas mixture is formed in the bubbles during pulsation, are very important here, naturally. Upon completion of this act the two variants of the medium are identical in principle from the standpoint of the mechanism of detonation wave generation.

The dynamics of a single cavity with a chemically active mixture was considered within the framework of the formulation of the problem of an "adiabatic" thermal explosion. The equation of pulsation in dimensionless form is

$$\beta d^2\beta/d\tau^2 + (3/2)(d\beta/d\tau)^2 = \bar{T}/\beta^3 - (d\beta/d\tau)/\beta\,\mathrm{Re} - \bar{p}, \tag{2}$$

where $\beta = R/R_0$ is the dimensionless radius, $\tau = t\sqrt{p_0/\rho_0}/R_0$; $\mathrm{Re} = R_0\sqrt{p_0\rho_0}/4\mu$, $\bar{T} = T/T_0$ is the temperature, and $\bar{p} = p_\infty/p_0$ is the pressure at infinity. The gas temperature inside the bubble was determined on the basis of the equation [11]

$$d\bar{T}/d\tau = \eta d\bar{N}/d\tau - 3(\gamma - 1)\bar{T}(d\beta/d\tau)/\beta. \tag{3}$$

Here $\eta = Q/(c_m T_0)$ is the heat of reaction Q relative to the initial temperature T_0 of the mixture and the molar heat capacity c_m of the gas, and $\bar{N} = N/A$ is the ratio of the concentration N of detonation products in the bubble to the initial concentration A of the initial material in it. This system is closed by the kinetic equation for the bimolecular reaction

$$d\bar{N}/d\tau = \zeta\beta^{-3}\sqrt{\bar{T}}\,e^{-\alpha/\bar{T}}(1 - \bar{N})^2, \tag{4}$$

where $\zeta = Az\sqrt{T_0}R_0/V_0\sqrt{p_0/\rho_0}$, $\alpha = E_a/BT_0$ is the activation energy E_a relative to the initial temperature T_0 and the universal gas constant B, z is a constant related to the radii r_1 and r_2 and masses m_1 and m_2 of the molecules by $z = N_0(r_1 + r_2)^2 \times [(8\pi B/N_0)(1/m_1 + 1/m_2)]^{1/2}$ (N_0 is the Avogadro number). Calculation showed that there exist minimum values $\bar{p}_{min} = \mathrm{const}$ of the amplitude at which the chemical reaction of the mixture in the bubble becomes explosive. For all the values of R_0 studied in the range 0.001-1 cm the time of the explosion did not coincide with the time when $\beta = \beta_{min}$ was reached but was in the initial stage of the phase of bubble expansion ($\dot{\beta} > 0$).

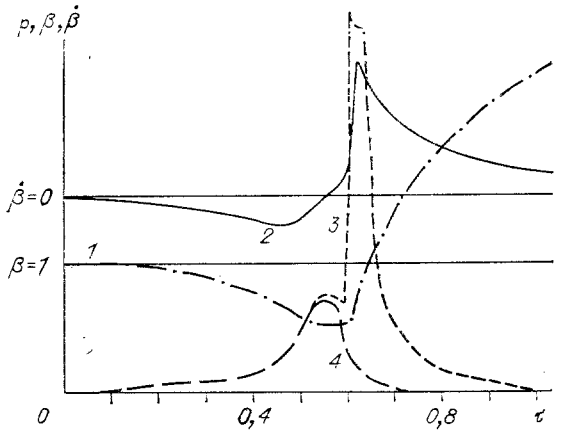

Fig. 5

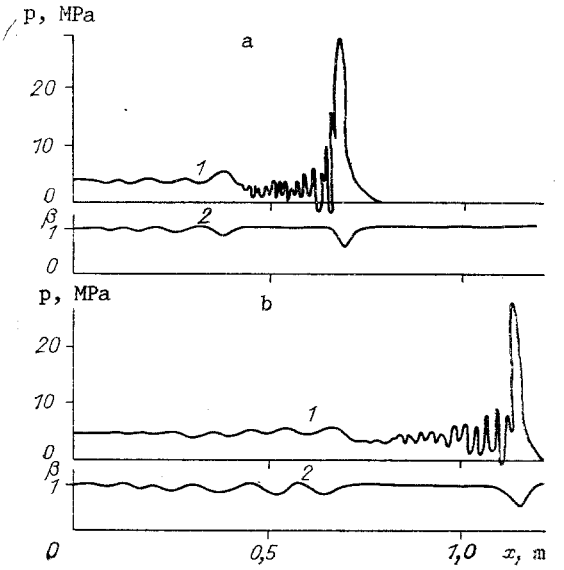

Fig. 6

Typical results of the behavior of $\beta(\tau) - 1$, $\dot{\beta}(\tau) - 2$, $\bar{p}_g(\tau) - 3$, $\bar{p}_{ad}(\tau) - 4$ are shown in Fig. 5, where the dynamics of the pressure in the mixture with respect to the pure "adiabatic curve" ($\bar{p}_{ad}$), without the kinetics. We note that up to the explosion $\bar{p}_b$ virtually follows $\bar{p}_{ad}$, i.e., the temperature increment due to the reaction is small. It is readily seen that the functions $\beta(\tau)$ and $\dot{\beta}(\tau)$ have kinks that are characteristic of an explosive load (see Fig. 1). In the neighborhood of the point of explosion the adiabatic component, obviously, no longer plays a role. Then the second terms on the right of Eq. (3) can be disregarded, whereby $\bar{T} \approx \eta \bar{N}$ and, therefore, the end of the reaction ($\bar{N} \to 1$) corresponds to the maximum temperature $\bar{T}_{max} = \eta$ (or $T = Q/c_m$). The dimensionless parameter η has a value of ~ 70 for the reaction under consideration.

It turned out that $\bar{p}_{min}$ decreases and the induction period (the time from the time of the collapse τ_* to the time of the explosion τ_0) increases as the initial radius R_0 of the bubble increases. We can obtain a corresponding estimate in the interval $\Delta\tau = \tau_0 - \tau_*$ by using Eq. (4) and assuming that in the region where the jump begins $\bar{N}$ can be neglected in comparison with 1 while β remains constant in this interval. Then, upon replacing $\bar{N}$ by $\bar{T}$ we have

$$d\bar{T}/d\tau \simeq \eta\zeta\beta_{min}^{-3}\sqrt{\bar{T}}\,e^{-\alpha/\bar{T}},$$

or, after rearrangements,

$$\tau_0 - \tau_* \simeq (2\beta_{min}^3/\eta\zeta)\int_{\sqrt{\bar{T}_*}}^{\sqrt{\eta}} e^{\alpha/y^2}\,dy. \qquad (5)$$

The upper limit is a constant characterizing the reaction, the lower limit is determined by the pressure at infinity, and $\zeta \sim R_0$. The estimate of the induction time, carried out in the particular case for $R_0 = 10^{-3}$ m and $\bar{p}_{min} = 4.1$ (lower threshold of the existence of an explosive reaction), when $\beta_{min} \approx 0.5$ and $T_* \approx 2.64$, gives $\Delta\tau \approx 1.8\cdot10^{-2}$, which accords completely with Fig. 5. The calculation was made for the parameters $\alpha \simeq 51.5$, $\eta \simeq 70$, $\zeta \simeq 2.72\cdot10^9\ R_0$. When p_{min} is exceeded $\Delta\tau$ decreases rapidly.

Wave propagation in a bubbled medium with the kinetics described above was studied numerically in the exact formulation in Lagrangian mass variables within the framework of the system

$$\begin{gathered}\rho_t = -\rho^2 u_s,\ u_t = -p_s,\\ \rho_0 R S_t + (3/2)\rho_0 S^2 = p_g - 2\sigma/R - 4\mu S/R - p,\\ T_t = QN_t/c_m A + 3(\gamma-1)q/c\rho_g R - 3(\gamma-1)TS/R,\\ N_t = 3z\sqrt{T}\,e^{-E_a/BT}(A-N)^2/4\pi R^3,\end{gathered} \qquad (6)$$

$$R_t = S,\ p_g = \rho_{0g}(R_0/R)^3 T(B/M),$$
$$p = p_0 + (\rho_0 c_0^2/n)((\rho/\rho_0(1-K))^n - 1),\ q = 2\pi R\lambda \mathrm{Nu}(T_0 - T),$$
$$\mathrm{Nu} = \begin{cases} \sqrt{\mathrm{Pe}}, & \text{if } \mathrm{Pe} > 100, \\ 10.0, & \text{if } \mathrm{Pe} < 100, \end{cases} \quad \mathrm{Pe} = 12(\gamma - 1) T_0 R |S|/\nu |T_0 - T|.$$

Here λ and ν are the thermal conductivity of the liquid and the thermal diffusivity of the gas, Pe is the Peclet number, c_0 is the velocity of sound in the liquid, s is the mass Lagrangian coordinate, M is the molecular weight in carbon units, $K = \frac{K_0\rho (R/R_0)^3}{\rho_0 (1 - K_0)}$ is the current value of the volume concentration, c is the heat capacity of the gas, ρ is the density of the mixture, and ρ_0 is the density of the liquid.

The result of the calculation for a hydrogen–oxygen mixture at a piston velocity of 3 m/sec, which initiates an incident wave, for a volume concentration $K_0 = 0.005$ and $R_0 = 0.2$ cm is shown in Fig. 6 for the times 500 μsec (a) and 1000 μsec (b) [curves 1) p(x), 2) $R/R_0 = \beta(x)$]. The amplitude of the "detonation leader" is about 30 MPa and the velocity is 1230 m/sec. The velocity of the fundamental wave decreases from 800 m/sec to 700 m/sec. Its front can be determined from the structure of the $\beta(x)$ distribution.

The velocity and amplitude of the detonation wave are stabilized: even at about 450 μsec the wave reaches a steady-state regime. The complete p(x) profile changes slightly: while at t = 500 μsec the detonation wave was virtually separated from the fundamental wave by some transitional zone of oscillations, by 1000 μsec the average amplitude of this zone had increased and had become comparable with the amplitude of the fundamental wave. The front of the latter, however, is determined fairly distinctly by the beginning of the second segment of the bubble pulsations (Fig. 6b, curve 2). This feature of the numerical solution is explained by the fact that the heat exchange of the bubble–liquid system is not taken into account completely. An estimate with an artificially intensified heat transfer supported this assumption: when the gas is cooled to the initial temperature the pressure in the medium returns to the initial value while the parameters of the detonation leader remain constant.

Comparison of the calculations with the experimental data confirms that the nonequilibrium two-phase model of a bubbled medium can be used to describe the principal parameters and the fine structure of real wave fields in processes with chemical transformations.

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