ACOUSTICS OF BOILING SOLUTIONS

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The possibility of an anomalous effect of the component composition on disturbance propagation in boiling solutions has been established. A criterion defining the cases in which the monotonic behavior of binary systems with respect to concentration is disturbed during sound propagation in them has been derived.

1. Fundamental Equations. The dynamics of bubbles in a liquid depends on the thermal conductivity and diffusion in the gaseous and the liquid phases and the inertia of the liquid as it moves around a bubble [1]. During the growth of vapor bubbles in superheated liquids, the inertia of the liquid hardly affects the process, which is determined only by the thermal conductivity and diffusion, which applies only to the liquid phase. This is connected with the fact that, in boiling liquids (in contrast to bubbles in cold liquids), equalization of the concentration of components and of the temperature occurs much faster within bubbles than in the liquid, and, therefore, the temperature and the concentrations of components within a bubble can be assumed to be uniform, always satisfying the equilibrium conditions, but changing in time. The theoretical basis for analyzing such a process is provided by Scriven's self-similar solution [2]. A survey of papers dealing with this problem is given in [1].

Under shock action on a solution where bubbles exist already or may develop, the behavior of bubbles in the liquid depends on the thermal, diffusion, and also inertial factors. A suitable formulation was presented and developed in [3]. The propagation of small disturbances in single-component, liquid—vapor bubble systems has been investigated in several papers, which are discussed in survey [4]. We should like to mention papers [5, 6] from among those not considered in [4].

We have investigated the propagation of acoustic disturbances in binary vapor—liquid bubble media.

Assume there is a binary liquid mixture containing spherical vapor bubbles of equal radius. One-velocity flow is contemplated. Then, in order to take into account the interphase heat and mass exchange, we use the equations of thermal conductivity and binary diffusion, written with an allowance for spherical symmetry within and around a sample bubble, and also a system of boundary conditions for these equations [4].

The system of macroscopic equations of phase mass conservation and of numerical concentration of bubbles for plane unidimensional motion in the linear approximation is given by [7]

$$\frac{\partial\rho_1}{\partial t}+\rho_{10}\frac{\partial v}{\partial x}=-J,\quad \frac{\partial\rho_2}{\partial t}+\rho_{20}\frac{\partial v}{\partial x}=J,\quad \frac{\partial n}{\partial t}+n_0\frac{\partial v}{\partial x}=0, \tag{1}$$

$$\rho=\rho_1+\rho_2,\ \rho_i=\rho_i^0\alpha_i,\quad \alpha_1+\alpha_2=1,\quad \alpha_2=\frac{4}{3}\pi a^3 n,\quad J=4\pi a_0^2 n_0 j. \tag{2}$$

The subscripts $i = 1, 2$ pertain to the liquid and vapor parameters, ρ_i, ρ_i^0, α_i, v, n, and a are the density averaged with respect to the mixture, the density averaged with respect to phase, the volumetric phase percentage, the velocity, the number of bubbles per unit volume of the mixture, and the bubble radius, respectively; J and j are the phase transition intensities, reduced to unit volume of the mixture and unit surface area of the interface, respectively. The parameters pertaining to the unperturbed state have the additional subscript 0.

Department of Physics and Mathematics, Bashkir Branch, Academy of Sciences of the USSR, Ufa. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 56, No. 5, pp. 709-715, May, 1989. Original article submitted November 12, 1987.

We write the momentum equation for the entire mixture,

$$\rho_0 \frac{\partial v}{\partial t} + \frac{\partial p_1}{\partial x} = 0 \tag{3}$$

and the equation of radial bubble variations in the linear approximation

$$a_0 \frac{\partial w_1}{\partial t} + 4\nu_1 \frac{w_1}{a_0} = \left(p_2 - p_1 + \frac{2\sigma}{a_0}\frac{a}{a_0}\right) \Big/ \rho_{10}^0. \tag{4}$$

Here, p is the pressure, w_i is the radial mass velocity of the phases at the bubble surface, and σ and ν_1 are the surface tension coefficient and the viscosity coefficient of the liquid.

The equations of thermal conductivity and diffusion are given by [3]:

$$\rho_{10}^0 c_1 \frac{\partial T_1'}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(\lambda_1 r^2 \frac{\partial T_1'}{\partial r}\right),$$

$$\frac{\partial g_{(1)1}'}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(D_1 r^2 \frac{\partial g_{(1)1}'}{\partial r}\right) \quad (r > a_0), \tag{5}$$

$$\rho_{20}^0 c_2 \frac{\partial T_2'}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(\lambda_2 r^2 \frac{\partial T_2'}{\partial r}\right) + \frac{\partial p_2}{\partial t},$$

$$\frac{\partial g_{(2)1}'}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(D_2 r^2 \frac{\partial g_{(2)1}'}{\partial r}\right) \quad (r < a_0). \tag{6}$$

Here, r is the microcoordinate [3], which represents the distance from the center of the bubble, T_i' is the phase temperature, $g_{(i)k}'$ is the mass concentration of the k-th component of the binary system in the i-th phase, λ_i and D_i are the coefficients of thermal conductivity and diffusion, respectively, and c_1 and c_2 are the specific heat values at constant pressure for the liquid and the vapor. The microparameters (i.e., the parameters which depend on r) are denoted by primes. The equation for T_2' is given without considering the term accounting for diffusion.

The equation of state for the phases is written in the following form:

$$p_1 = p_{10} + C_1^2(\rho_1^0 - \rho_{10}^0), \quad p_2 = \rho_2^{0'} R T_2' (g_{(2)1}'/\mu_1 + (1 - g_{(2)1}'/\mu_2), \tag{7}$$

where C_1 is the velocity of sound in the liquid, R is the universal gas constant, and μ_i are the molecular weights of the components. We also assume that Dalton's law [8] and the equal-pressure condition ($p_2' = p_2$) [3] hold for the vapor components of an imperfect solution:

$$p_2 = \gamma_1 p_{s(1)}(T_a) N_{(1)1a} + \gamma_2 p_{s(2)}(T_a)(1 - N_{(1)1a}), \quad N_{(i)k}' = \frac{\mu_2 g_{(i)k}'}{\mu_2 g_{(i)k}' + \mu_1(1 - g_{(i)k}')}. \tag{8}$$

Here, $p_{s(k)}$ is the saturation pressure of the pure k-th component, $N_{(i)k}'$ is the molar concentration of the k-th component in the i-th phase, and γ_1 and γ_2 are the activity coefficients. The subscript a signifies that the parameter values pertain to the interface between phases. The Clapeyron–Clausius relationships hold for partial pressures of the components,

$$\frac{dp_{s(k)}}{dT_a} = \frac{\mu_k l_k p_{s(k)}}{R T_a^2}, \quad k = 1,\ 2, \tag{9}$$

where ℓ is the specific heat of vaporization.

The equilibrium conditions for the unperturbed state are

$$T_{10} = T_{20} = T_0, \quad p_{20} = p_{10} + 2\sigma/a_0,$$

$$p_{20} = \gamma_1 p_{s(1)}(T_0) N_{(1)10} + \gamma_2 p_{s(2)}(T_0)(1 - N_{(1)10}). \tag{10}$$

The boundary conditions at the mobile boundary – the interface between phases – are written thus:

$$T_1 = T_2 = T_a, \quad j_1 l_1 + j_2 l_2 = \lambda_1 \frac{\partial T_1'}{\partial r} - \lambda_2 \frac{\partial T_2'}{\partial r},$$

$$g_{(1)10} j_2 - (1 - g_{(1)10}) j_1 = -\rho_{10}^0 D_1 \frac{\partial g_{(1)1}'}{\partial r},$$

$$g_{(2)10} j_2 - (1 - g_{(2)10}) j_1 = -\rho_{20}^0 D_2 \frac{\partial g_{(2)1}'}{\partial r}, \tag{11}$$

$$\rho_{10}^0 \left(\frac{\partial a}{\partial t} - w_1 \right) = \rho_{20}^0 \left(\frac{\partial a}{\partial t} - w \right) = j, \quad j = j_1 + j_2 \quad (r = a_0).$$

It is assumed that the heat of component mixing is much lower than the vaporization heat. Moreover,

$$\frac{\partial T_2'}{\partial r} = 0, \quad \frac{\partial g_{(2)1}'}{\partial r} = 0 \quad (r = 0). \tag{12}$$

For the closure of the system of boundary relationships, it is necessary to assign one more condition each for T_1' and $g_{(1)1}'$. If the drops in temperature and concentration in the liquid near the phase interfaces occur at distances much smaller than the distance between bubbles, we can assume that

$$r \to \infty: \quad T_1' = T_0, \quad g_{(1)1}' = g_{(1)10}. \tag{13}$$

If these distances are comparable to each other, the adiabatic conditions and an absence of mass exchange between spherical cells [5] are more appropriate:

$$r = \frac{a_0}{\alpha_{20}^{1/3}}: \quad \frac{\partial T_1'}{\partial r} = 0, \quad \frac{\partial g_{(1)1}'}{\partial r} = 0. \tag{14}$$

We seek the solution of the reduced system in the form of a damped traveling wave:

$$p, \ v, \ w, \ n, \ a \sim \exp[i(Kx - \omega t)], \quad T' = T(r) \exp[i(Kx - \omega t)],$$

$$g' = g(r) \exp[i(Kx - \omega t)], \quad K = k + i\delta, \tag{15}$$

where δ is the damping coefficient, and $C = \omega/k$ is the phase velocity. On the basis of the condition for the existence of this type of solution, we obtain the following dispersion relation [for boundary conditions in the form of (14)]:

$$\frac{K^2}{\omega^2} = \rho_0 \left(\frac{\alpha_{10}}{\rho_{10}^0 C_1^2} + 3 \frac{\alpha_{20}}{\psi} \right), \quad \psi = 3\gamma p_{20} \Pi^{-1} - \rho_{10}^0 \omega^2 a_0^2 - 4i\rho_{10}^0 \nu_1 \omega - 2\sigma/a_0, \tag{16}$$

$$\Pi = 1 + (\gamma - 1)(1 - \chi_1) \Pi_2(y_2) + \gamma [\chi_{12} \varepsilon_\rho^{-1} \Pi_1(z) A_g + ((\chi_1 - 1) \Pi_2(y_2) + \chi_1 \eta \Pi_1(y_1)) A_T] A^{-1},$$

$$A_T = \chi_1 \varepsilon_\rho^{-1} \Pi_1(z_1) + \frac{g_{(2)10}(1 - g_{(2)10})}{g_{(1)10}(1 - g_{(1)10})} \chi_2 \Pi_2(z_2) -$$

$$- \left(1 - \frac{1}{\gamma}\right) (g_{(2)10} - g_{(1)10}) \chi_1 \chi_2 \Pi_2(y_2),$$

$$A_g = (g_{(2)10} - g_{(1)10}) \chi_1 [\chi_2 \eta \Pi_1(y_1) + (\chi_2 + 1) \Pi_2(y_2)] +$$

$$+ g_{(2)10}(1 - g_{(2)10}) \chi_2 \Delta \Pi_2(z_2),$$

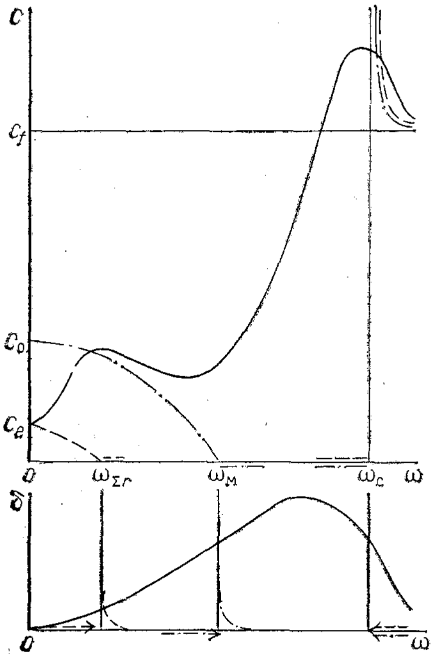
$$A = \frac{(g_{(2)10} - g_{(1)10})(N_{(2)10} - N_{(1)10})}{g_{(1)10}(1 - g_{(1)10})} \chi_1 \chi_2 (\eta \Pi_1(y_1) + \Pi_2(y_2)) +$$

$$+ \left(\frac{\chi_1}{\chi_2} \varepsilon_\rho^{-1} \Pi_1(z_1) - \frac{g_{(2)10}(1 - g_{(2)10})}{g_{(1)10}(1 - g_{(1)10})} \frac{\chi_2}{\chi_1} \Pi_2(z_2) \right) \left(1 - \frac{1}{\gamma}\right),$$

$$\Pi_1(x) = 3[1 - x(Mx \operatorname{th} x(M-1) - 1)(Mx - \operatorname{th} x(M-1))^{-1}] x^{-2},$$

$$\Pi_2(x) = 3(x \operatorname{cth} x - 1) x^{-2}, \quad \gamma = c_{2p}/c_{2v}, \quad \varepsilon_\rho = \rho_{20}^0/\rho_{10}^0,$$

$$\chi_i = \frac{c_2 T_0}{L_i}, \quad \chi_{12} = \frac{l_2 - l_1}{L_1}, \quad \eta = \varepsilon_\rho^{-1} \frac{c_1}{c_2}, \quad \Delta = \frac{l_2 \mu_2 - l_1 \mu_1}{RT_0},$$



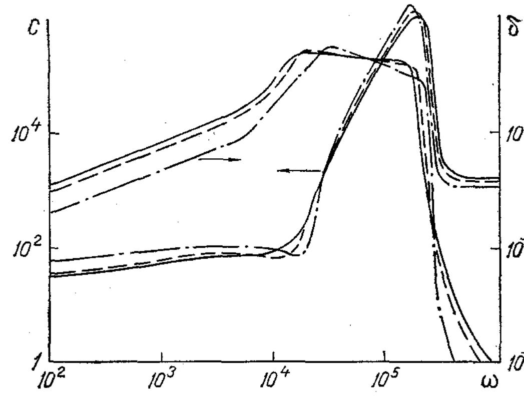


Fig. 1 Fig. 2

Fig. 1. Qualitative dependences of the phase velocity of sound C and the damping decrement δ on the frequency ω in a bubble vapor–liquid medium.

Fig. 2. Phase velocity and the damping coefficient of sound in an aqueous solution of ethanol containing vapor bubbles; C (m/sec); ω (sec^{-1}); δ (m^{-1}).

$$L_i = l_1 g_{(i)10} + l_2 (1 - g_{(i)10}), \quad M = \alpha_{20}^{-1/3},$$

$$\varkappa_i = \frac{\lambda_i}{\overset{0}{\rho}_{i0} c_i}, \quad y_i = \sqrt{-i\,\frac{\omega a_0^2}{\varkappa_i}}, \quad z_i = \sqrt{-i\,\frac{\omega a_0^2}{D_i}} \quad (i = 1,\ 2).$$

We have written the expression for Π by neglecting unity in comparison with ε_ρ^{-1}. The form of the $\Pi_1(x)$ function presented corresponds to boundary conditions (14), while, for (13) we have

$$\Pi_1(x) = 3(1 + x)x^{-2}.$$

2. Calculation Results. Figure 1 shows schematically the dependences corresponding to (16): the phase velocity of sound C and the damping coefficient δ as functions of the frequency ω of forced oscillations (ω-waves), generated by an external source, in a vapor–liquid bubble medium which is in equilibrium in the initial state. The solid curves correspond to the most characteristic media in states remote from the critical state. The dashed curves, defined by C_e and $\omega_{\Sigma r}$, where

$$C_e = \frac{\overset{0}{\rho}_{20} L_2 \sqrt{1 - \Sigma'}}{\overset{0}{\rho}_{10} \sqrt{c_1 T_0}\, \alpha_{10} \sqrt{1 + \beta_1}}, \quad \omega_{\Sigma r} = a_0^{-1} \sqrt{\frac{2\sigma\gamma_\Sigma}{a_0 \overset{0}{\rho}_{10}}},$$

$$\gamma_\Sigma = \frac{1}{\Sigma'} - 1, \quad \Sigma' = \frac{\beta \Sigma \alpha_{10}}{(1 + \beta_1)\alpha_{20}}, \quad \Sigma = \frac{2\sigma}{3\gamma p_{20} a_0},$$

$$\beta = (\gamma - 1)\chi_2^2 \eta, \quad \beta_1 = \left(1 - \frac{1}{\gamma}\right) \frac{(g_{(2)10} - g_{(1)10})(N_{(2)10} - N_{(1)10})}{g_{(1)10}(1 - g_{(1)10})} \chi_2^2 \frac{c_1}{c_2},$$

correspond to the one-temperature (homothermic), dissipation-free scheme with uniform concen-

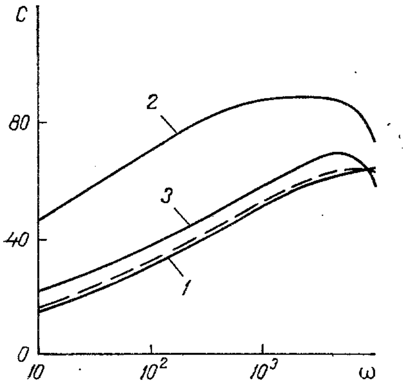


Fig. 3

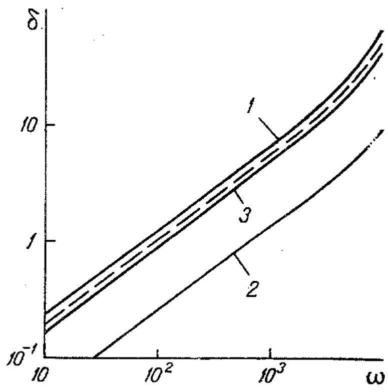


Fig. 4

Fig. 3. Phase velocity of sound in an aqueous solution of ethylene glycol containing vapor bubbles.

Fig. 4. Coefficient of sound damping in an aqueous solution of ethylene glycol containing vapor bubbles.

trations and uniform and equal phase temperatures in a cell ($\nu_1 = 0$; $D_1 = D_2 = \infty$; $\lambda_1 = \lambda_2 = \infty$). The dash–dot curves, defined by C_0 and ω_M, where $C_0 = \sqrt{\gamma p_0/\rho_{10}{}^0\alpha_{10}\alpha_{20}}$, $\omega_M = a_0{}^{-1}\sqrt{3\gamma p_0/\rho_{10}{}^0}$, and $p_0 \simeq p_{10} \simeq p_{20}$ correspond to a dissipation-free scheme without thermal conductivity and diffusion ($\nu_1 = 0$, $D_1 = D_2 = 0$, and $\lambda_1 = \lambda_2 = 0$). Abnormally heavy damping of disturbances occurs in the frequency range $\omega_M \leq \omega \leq \omega_C$ ($\omega_C = \omega_M\sqrt{1 + \alpha_{20}/\alpha_{2*}}$, $\alpha_{2*} = \gamma p_0/\rho_{10}{}^0 C_1{}^2$).

Figure 2 shows the phase velocity and the damping coefficient as functions of the frequency for an aqueous solution of ethanol for $p_{10} = 0.1$ MPa, $\alpha_{20} = 10^{-2}$, $a_0 = 10^{-3}$ m. The solid curve corresponds to a vapor–water mixture ($g_{(1)10} = 1$), the dashed curve pertains to a solution with $g_{(1)10} = 0.5$, while the dash–dot curve corresponds to $g_{(1)10} = 0$. It is evident here that the curves corresponding to a binary system lie between the curves for pure components. For $g_{(1)10} = 0.5$, we have $C_e = 0.6$ m/sec, $\omega_{\Sigma r} = 10^2$ sec^{-1}, $C_0 = 118$ m/sec, and $\omega_M = 2 \cdot 10^4$ sec^{-1}. Figures 3 and 4 provide the phase velocity and the damping coefficient as functions of the frequency for an aqueous solution of ethylene glycol for $p_0 = 0.1$ MPa, $\alpha_{20} = 10^{-2}$, and $a_0 = 10^{-3}$ m. Curves 1-3 correspond to a vapor–water mixture ($g_{(1)10} = 1$), an aqueous solution of ethylene glycol ($g_{(1)10} = 0.05$), and pure ethylene glycol containing vapor ($g_{(1)10} = 0$), respectively, while the dashed curves pertain to calculation based on the diffusion-equilibrium model ($D_1 = \infty$).

It is evident that, in the case of aqueous solutions of ethylene glycol, the damping and dissipation of sound in the solution, calculated with respect to the actual value of the diffusion coefficient, do not lie between the limiting values calculated for pure components. This is connected with the cardinal effect of diffusion in the liquid phase on the phase transition intensity (the diffusion resistance effect). In the variant calculated above, for a water concentration of only 5% in the solution, the water vapor concentration in the vapor phase reaches 85%. Therefore, it is clear that the phase transition intensity is limited by the ability of the water component to diffuse through the less volatile ethylene glycol.

However, it would be important to find a quantitative criterion which would define the cases where a "diffusion lag" of phase transitions occurs, where one could expect that the monotonic behavior of binary systems with respect to concentration during sound propagation in them would be disturbed.

An analysis of the dispersion relation and numerical calculations indicate that we can assume the following for many binary media:

$$A_T = \chi_1\varepsilon_\rho^{-1}\Pi_1(z_1), \quad A_g = (g_{(2)10} - g_{(1)10})\chi_1\chi_2\eta\Pi_1(y_1),$$

$$A = \frac{\chi_1}{\chi_2}\varepsilon_\rho^{-1}(1-\gamma^{-1})^{-1}\Pi_1(z_1) + \frac{(g_{(2)10} - g_{(1)10})(N_{(2)10} - N_{(1)10})}{g_{(1)10}(1 - g_{(1)10})}\chi_1\chi_2\eta\Pi_1(y_1).$$

Then, the expression for Π, which is responsible for nonequilibrium heat and mass exchange in the dispersion equation, assumes the following form:

$$\Pi = 1 + \beta\Pi_1(y_1)[1 + \beta_1\Pi_1(y_1)\Pi_1^{-1}(z_1)]^{-1},$$
$$\beta = (\gamma - 1)\chi^2\eta, \quad \beta_1 = \left(1 - \frac{1}{\gamma}\right)\frac{(g_{(2)10} - g_{(1)10})(N_{(2)10} - N_{(1)10})}{g_{(1)10}(1 - g_{(1)10})}\chi_2^2\frac{c_1}{c_2}. \tag{17}$$

Consequently, we can neglect the nonequilibrium thermal and diffusion processes within bubbles, and dissipation within the system is then basically determined by the problem of external heat and diffusion.

The following asymptotic behavior holds for the function $\Pi_1(x)$ in the frequency range pertaining to the curves of Figs. 2-4:

$$\Pi_1(x) = 3/x, \quad |x| \gg 1,$$

and, thus,

$$1 + \beta_1\Pi_1(y_1)\Pi_1^{-1}(z_1) = 1 + \beta_1\sqrt{\varkappa_1/D_1} = 1 + \beta_2.$$

If the addition β_2 due to the nonequilibrium diffusion process in the liquid is small ($\beta_2 \ll 1$), the diffusion lag of phase transitions does not occur, and we use the dispersion expression for single-component, vapor–liquid bubble media with the effective characteristics to determine the phase velocity and the damping coefficient. For the specific vaporization heat, we should use its mean-mass value with regard to the vapor phase.

In binary systems where $\beta_2 \gtrsim 1$, we can expect the diffusion resistance effect, which reduces the rate of phase transitions and, thus, leads to the anomalous effect of the component composition on the propagation of disturbances in boiling solutions. For the above binary systems (aqueous solutions of ethanol and ethylene glycol), the values of the β_2 parameter where equal to 0.1 and 7.7, respectively.

In view of the difficulties involved in direct experimental determination of the concentration and the mutual diffusion coefficient in solutions, it would be interesting to determine them indirectly by measuring the damping and the velocity of sound in binary vapor–liquid media with a bubble structure.

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