SOUND VELOCITY AND PARAMETER OF NONLINEARITY OF A TERNARY MIXTURE CONSISTING OF WATER, VAPOUR AND DRY AIR

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Acoustic properties of a binary mixture consisting of a liquid being in phase equilibrium with its vapor and a ternary mixture including a binary one and a neutral gas are considered. Detailed calculations of the excess entropy of a ternary mixture in terms of its excess pressure and density are carried out with accuracy up to quadratic nonlinear terms. That allows to estimate the small signal sound velocity and the parameter of nonlinearity $B/A$ of the mixture as a whole. The only assumption is that the vapor and the neutral gas are ideal gases. As an example, the ternary mixture consisting of air and water being in equilibrium with its vapor is considered. Two different kinds of ternary mixtures are considered, one associated with the mixture in which the vapor and air occupy a mutual volume, and another associated with a mixture in which the gases occupy the separate volumes.

Key words: ternary mixtures, phase equilibrium, parameter of nonlinearity.

1. Introduction

A simplest multi-component fluid mixture consists of immiscible fluids under the equal pressure without chemical reactions and phase transitions. The mixture as whole is a homogeneous continuity. Evaluations of acoustic quantities are based on the relations of superposition of specific volumes and variations in entropy per unit mass of every compound [1]. Final expressions for the sound speed and parameter of nonlinearity tend to that in a pure phase when the mass concentrations of all other compounds tend to zero.

Another important medium of sound propagation is a bubbly liquid. Extend literature on this subject exists [2, 3]. The theory of sound in bubbly media is based on dynamic equations of a single oscillator, which is the gas bubble. The problem itself is very complex, in view of liquid boundaries, the thermal and pressure regime inside
A bubble, account of heat and mass transfer between the bubble and liquid. A bubble includes in general both air and vapor of the liquid, and vapor is known to influence the bubble resistance. The dynamic equation of a bubble is highly nonlinear. Next, an ensemble of oscillators is involved into the equations of conservation of the fluid as a whole. In other words, the presence of a bubble essentially adds nonlinearity and makes the flow disperse. The dynamics of a bubbly liquid is mostly governed by the difference in compressibility of the liquid and gas, though it depends on mass and heat transfer [3].

The subject of this paper are not bubbly liquids or homogeneous mixtures consisting of immiscible fluids, but media in which heat and mass transfer in the phase equilibrium takes place. Thus the general conclusions about the character of nonlinear dynamics of sound and sound velocity have nothing in common with the two problems mentioned before. We consider sound propagation over mixtures consisting of a neutral gas and a liquid being in phase equilibrium with its vapor. The problem needs the involving of thermodynamics of a binary mixture consisting of a liquid being in phase equilibrium with its vapor, and a proper account of isentropic equilibrium processes of the ternary mixture. The mixture is treated as a homogeneous continuity, that means that every small volume includes all compounds accordingly to their concentrations, and that the sound wavelength is much greater than the characteristic scale of inhomogeneity. In contrast to multi-component systems of immiscible fluids, neither the velocity of sound nor the parameter of nonlinearity in binary mixtures (consisting of liquid and its vapor being in the phase equilibrium) head toward a limit of those values in pure phases when the corresponding mass concentrations head for zero. The problem also does not need the involving of an ensemble of oscillators. In contrast to a bubbly liquid, a ternary mixture under consideration is not dispersive.

A complete investigation has never been undertaken. The reason for it are the mathematical difficulties in computing the nonlinear features of sound propagation, and, probably, the lack of scientific interest for this special kind of media. On the other hand, the problem is subdivided into two different ones: under some special conditions listed in Subsecs. 3.1 and 3.2 below, both the gases may occupy separate volumes or the same volume.

Thermodynamic features of a binary mixture consisting of a liquid and its vapor are the foundation of further calculations of both kinds of ternary mixtures. There have been reported basic results on thermodynamic features of binary mixtures [4, 5] basing on the following limitations: 1) the liquid is incompressible; 2) the specific heat at constant volume of the liquid is constant; 3) the heat of vaporization is constant; 4) the density of the liquid is considerably larger than that of its vapor; 5) the vapor is an ideal gas. The analysis undertaken by the author reveals that the conditions 1–5 result in satisfying accuracy of the computations of sound velocity, but like the computations of the parameter of nonlinearity, at least the first four ones should be revised [6]. Moreover, the limitations 1, 3, 4 and 5 result in an equality of the capacities under the constant pressure of water and its vapor, which will be proved in the Sec. 2. This contradicts the experimental data. The author uses only the fifth limitation in all the estimations below.
Since a binary mixture is a part of the ternary one, accurate evaluations are of great importance. This concerns especially the estimates of parameters of nonlinearity $B/A$, $C/A$ and higher ones.

2. Governing equations, sound velocity and the parameter of nonlinearity for a binary mixture consisting of water being in phase equilibrium with its vapor

Let us consider a binary mixture consisting of a liquid and its vapor being in phase equilibrium. The starting points of thermodynamics of a binary mixture are the following equations. The density of the mixture $\rho_{1,2}$ is related to the densities of the liquid and vapor $\rho_1, \rho_2$ as follows ($x$ means mass concentration of the vapor):

$$\frac{1}{\rho_{1,2}} = \frac{1-x}{\rho_1} + \frac{x}{\rho_2}. \quad (1)$$

The vapor is an ideal gas in accordance to the fifth condition of the introduction and obeys an equality:

$$\rho_2 = \frac{\mu_2 p_2}{RT}. \quad (2)$$

Index 1 stands for quantities referring to the liquid, index 2 to those of the vapor, and the index 1, 2 to those of the mixture as a whole, $\mu_1 = \mu_2$ is the molar mass, $R$ is the universal gas constant. In the area of phase equilibrium, the pressure is the same for both the phases and satisfies the equation of Clapeyron [4, 5]:

$$\frac{dp_1}{dT} = \frac{dp_2}{dT} = \frac{\Delta s}{\mu_2(1/\rho_2 - 1/\rho_1)}, \quad (3)$$

where the difference in their molar entropies is expressed in terms of the enthalpy of vaporization of the liquid in the following way:

$$\Delta s = s_2 - s_1 = \frac{\Delta H}{T}, \quad (4)$$

$\Delta H$ is the enthalpy (the heat) of vaporization, a quantity slightly depending on temperature. Equations (1)–(4) along with the following relations for the partial and summary changes of the entropy (5) form an initial point for further calculations:

$$s'_{1,2} = (1-x)s'_1 + xs'_2 + x\Delta s,$$

$$s'_1 = \frac{\gamma_1 C_{V,1}}{T_\beta_1} \left( p'_2 - c_1^2 \rho_1 - \left( \frac{B}{2A} \right) \frac{c_1^2}{\rho_1} \rho_1'^2 \right),$$

$$s'_2 = \frac{C_{V,2}}{p_2} \left( p'_2 - c_2^2 \rho_2 - \left( \frac{B}{2A} \right) \frac{c_2^2}{\rho_2} \rho_2'^2 \right), \quad (5)$$
where \( p', \rho', s', x' \) denote excess quantities, \( C_V, \gamma, \beta \) mean molar heat capacity under constant volume and compressibility under constant pressure and volume, respectively, and \( c \) denotes a small signal sound velocity in the pure phase. Equations (1)–(5) expanded in Taylor series by taking into account the phase equilibrium, result finally in the excess entropy of a binary mixture expressed in terms of its excess pressure and density:

\[
 s'_{1,2} = K_{1,2} \left( p'_2 - c^2_{1,2} \rho'_2 \rho_{1,2} - \left( \frac{B}{2A} \right) \frac{c^2_{1,2} \rho'_2 \rho_{1,2}^2}{\rho_{1,2}} \right), \tag{6}
\]

where \( K_{1,2}, c_{1,2} \) and \( (B/A)_{1,2} \) are some functions of concentration of the vapor, temperature and other equilibrium quantities computed by the author. It would be useful to write down an expression for the square sound velocity of a binary mixture:

\[
 c^2_{1,2} = \frac{\Delta H \mu_2 p_2 / (RT^2 \rho_2^2)}{x \left( - \frac{2R}{p_2} + \frac{\Delta H}{p_2 T} + \frac{C_{p,2} RT}{\Delta H p_2} \right) + (1-x) \left( - \frac{2\beta_1 \mu_2}{\rho_1} + \frac{\gamma_1 \Delta H p_2 \mu_2}{RT^2 \rho_1^2} + \frac{C_{p,1} RT}{\Delta H p_2} \right)}. \tag{7}
\]

Compared to the well-known results [4, 5], the formula (7) includes the terms

\[
 - \frac{2\beta_1 \mu_2}{\rho_1} + \frac{\gamma_1 \Delta H p_2 \mu_2}{RT^2 \rho_1^2},
\]

which play a role for extremely small concentrations of the vapor. The quantities \( (B/A)_{1,2} \) and \( K_{1,2} \) are not presented in the text because of the long expressions involved, they may be found together with details of the corresponding calculations concerning a binary mixture in paper [6].

Calculations of a small-signal sound velocity \( c_{1,2} \) and the parameter of nonlinearity \( (B/A)_{1,2} \) have been undertaken by the author basing on a mixture consisting of water and its vapor being in phase equilibrium. The equilibrium data relate to the temperature \( T = 373.15 \) K and pressure \( p_2 = 1 \) atm [7, 8]. The small-signal sound velocity \( c_{1,2} \) is a linear quantity, and as expected, it agrees very well with results of other authors. To compare results, the data of Arutunian [5] and Kuznetsov [9] were used. In the paper of Kuznetsov, there is an empiric equation of state for the internal energy of water, which may be transformed into the following one:

\[
 E = 4.1868 \cdot 10^3 \left( 71326.1 \mu^{0.245} + 6.82997 \cdot 10^6 \rho^{7/8} / \rho \right), \tag{8}
\]

where the quantities \( \mu, \rho \) are in Pa and kg/m\(^3\), respectively and \( E \) is in J/kg. The small-signal sound velocity and the parameter of nonlinearity were calculated by the author basing on formula (8) and known thermodynamic relations. Figure 1 presents a small-signal sound velocity calculated on the basis of (7) and accordingly to Arutunian [5] (a difference is not noticeable, the thin line), and accordingly to the empiric equation of state given by Kuznetsov (the bold line). The sound velocity quickly decreases with decrease of the vapor fraction in the mixture; when \( x \) tends toward zero, it tends toward 1.1 m/s. It is clear that there is neither analogy to immiscible fluids, nor to water including pure vapor bubbles.
The analysis undertaken by the author reveals a noticeable difference of the quantities \( B/A \) and those obtained under the limitations recalled in the introduction. Results of the author, based only on the fifth limitation, achieve greater values over the domain of \( 0.1 < x < 1 \), and coincide well for lower concentrations. It is remarkable, that the predictions by Arutunian give negative values of \( B/A \) over the whole domain of \( x \). The difference between the present study and the results reported by Arutunian is caused by the limitations listed in the introduction which were used by Arutunian. Let us prove, that limitations the 1, 3, 4, 5 of the introduction lead to the an equality of the capacities under constant pressure of water and its vapor, contradicting the experimental data [7]. Indeed, assuming that \( \Delta H(p(T), T) \) is at phase equilibrium a function of temperature, it follows from (4):

\[
\frac{d(\Delta H)}{dT} = T \left[ \left( \frac{\partial s_2}{\partial p} \right)_T - \left( \frac{\partial s_1}{\partial p} \right)_T \right] \frac{dp}{dT} + \left( \frac{\partial s_2}{\partial T} \right)_p - \left( \frac{\partial s_1}{\partial T} \right)_p \right] + s_2 - s_1
\]

\[
= T \left( C_{p,2} - C_{p,1} \right) - \mu_2 \left[ \left( \frac{\partial V_2}{\partial T} \right)_p - \left( \frac{\partial V_1}{\partial T} \right)_p \right] \frac{dp}{dT} + \frac{\Delta H}{T}.
\]

(9)

The well-known relationships of thermodynamics are used:

\[
\left( \frac{\partial s}{\partial p} \right)_T = -\mu \left( \frac{\partial V}{\partial T} \right)_p,
\]

\[
T \left( \frac{\partial s}{\partial T} \right)_p = C_p,
\]

(10)

where \( V = 1/\rho \) is the specific volume. The incompressibility of water, its small specific volume compared to that of the gas, and the equation of state for the vapor as an ideal gas (limitations 1, 4, 5) give:

\[
\left( \frac{\partial V_1}{\partial T} \right)_p = 0,
\]

\[
\frac{dp}{dT} = \frac{\Delta H}{\mu_2 T(V_2 - V_1)} \approx \frac{\Delta H}{\mu_2 T V_2},
\]

\[
\frac{1}{V_2} \left( \frac{\partial V_2}{\partial T} \right)_p = \frac{1}{T},
\]

(11)

that together with (9) results in the following equation:

\[
\frac{d(\Delta H)}{dT} = C_{p,2} - C_{p,1}.
\]

(12)

Thus, if the heat of vaporization does not depend on temperature (limitation 3), the heat capacities should be equal, that is contradictory to the experimental data. For example, the heat capacity of water under the pressure of one atmosphere and at temperature 100° C is 76 J/mol·K, and that of its vapor is 33 J/mol·K [7].

In the present study, the only limitation is that the vapor is ideal. Since the results are highly sensitive to the curvature of the equation of state (its second derivatives), it is not surprising, that the calculations of \( B/A \) basing on the empirical formula of Kuznetsov (8) are not reliable. They give approximately a uniform \( B/A = 0.14 \) over \( 0 < x < 1 \).

The coefficient of nonlinearity \( \varepsilon = B/2A + 1 \) remains positive over all the domain of the mixture existing for both sets of calculations (Arutunian and Perelomova). The lowest value which it achieves is about \( \varepsilon = 0.012 \) while \( x \) tends toward zero.
Thus the general conclusions are that the character of the nonlinear distortions in the binary mixture does not vary ($c(v) = c + \varepsilon v$, where $v$ is velocity of particles, and $c$ is the velocity of the infinitely small amplitude sound). The sound velocity is considerably less than that in pure water for any $x$. The nonlinear distortions are weaker in comparison to those in pure water ($B/A_1 \approx 6.1$ [7]). It should be noticed once again that the limit of the pure phase dynamics $x$ does not exist when $x$ tends toward 0 or 1.

3. Sound velocity and parameter of nonlinearity of ternary mixtures with separate or mutual volumes occupied by a neutral gas

Equation (6) is a foundation of further evaluations concerning three-compound mixtures. Going to the ternary mixtures by involving of a neutral gas, two basic types of mixtures should be considered. The first one is related to a mixture with a mutual volume occupied by the neutral gas and the vapor, while the second one deals with separate volumes of both the gases. Each one of these different kinds of mixtures needs the including of additional physical conditions for the problem to be well-proved. The quantities related to a neutral gas will be denoted by the index 3 everywhere in the text below, and those related to the mixture as a whole have not indices.

All the compounds of every type of a ternary mixture are in the thermodynamic equilibrium and at equal temperatures. The excess entropy of the unit mass of the ternary mixtures of every kind is additive:

$$T = T_1 = T_2 = T_3, \quad S' = x_3 s'_3/\mu_3 + (1 - x_3) s'_{1,2}/\mu_1,$$

where $s'_3$, $s'_{1,2}$ denote the changes in molar entropy of the neutral gas and the binary mixture, $S'$ denotes the excess entropy per mass unit of the whole mixture, $x_3$ is the
constant mass concentration of the neutral gas. The mass concentration of air in the ternary mixture $x_2$ is related to the concentration of the vapor in the binary mixture $x$ in the following manner:

$$x_2 = (1 - x_3)x.$$  \hspace{1cm} (14)

### 3.1. Additional conditions for the mixture with mutual volume of the vapor and neutral gas

The pressure of the mixture with mutual volume of gases equals to a sum of the partial pressures of every gas, which are treated as ideal gases:

$$p = \sum_{i=2,3} p_i, \quad p_i = \frac{R\rho_i T}{\mu_i}. \hspace{1cm} (15)$$

Equations (15) yield the partial pressure of every gas:

$$p_2 = p \frac{x_2 \mu_3}{x_2 \mu_3 + x_3 \mu_2} = p - p_3. \hspace{1cm} (16)$$

The next condition takes into account the mutual volume occupied by both the gases:

$$\rho = \frac{\rho_{1,2}}{1 - x_3}. \hspace{1cm} (17)$$

A complete vaporization in the mixture in which the gases occupy a mutual volume, never may occur [5], i.e. $x < 1$, and therefore,

$$x_2 < \frac{\mu_2}{\mu_3(p/p_2 - 1) + \mu_2}. \hspace{1cm} (18)$$

### 3.2. Additional conditions for the mixture with separate volumes of the vapor and neutral gas

The pressure of the mixture with separate volumes of the gases equals each partial pressures:

$$p = p_1 = p_2 = p_{1,2} = p_3, \hspace{1cm} (19)$$

which, together with the equality of temperature of all the compounds, yields the relationship

$$\frac{p_2}{\mu_2} = \frac{p_3}{\mu_3}, \hspace{1cm} (20)$$

considerably simplifying further calculations. It follows from $0 \leq x \leq 1$ and (14) that

$$0 \leq x_3 \leq 1 - x_2. \hspace{1cm} (21)$$
Additional links provided by each type of ternary mixtures should be expanded in the Taylor series with an accuracy up to the second order nonlinear terms. They yield in a following relation for the excess entropy of the ternary mixture as a whole like (6):

\[ s' = K \left( p' - c^2 \rho' - \left( \frac{B}{2A} \right) \left( \frac{c^2}{\rho} \rho' \rho'' \right) \right), \tag{22} \]

with quantities \( K, c \) and \( B/A \) representing a three-parametric family of functions depending in general on the concentrations of the vapor and neutral gas in the ternary mixture, \( x_2 \) and \( x_3 \), pressure \( p \) and the equilibrium thermodynamic values. Every type of mixtures possesses obviously its own set of functions. The author with help of Mathematica derived explicit expressions for all these quantities. However they are too complex to be presented in this text.

4. Examples of computations of sound velocity and parameter of nonlinearity of the ternary mixture consisting of water, its vapor and dry air

The evaluations of the sound velocity and parameter of nonlinearity for mixtures with separate volumes of the vapor and neutral gas are considerably easier than of those for mixtures with mutual volume occupied by the gases. The mixtures of this kind may exist under very special conditions, when water particles become moistened by a non-fleeting liquid or intense heating takes place [5].

Some curves for the ternary mixture consisting of water, its vapor and dry air calculated by use of (22), are presented in Figs. 2, 3. The equilibrium data are related to the temperature \( T = 373.15 \) K and pressure \( p_2 = 1 \) atm [7, 8].

The curves in Fig. 2 occupy the domain of existence of the ternary mixture with separate volumes occupied by air and vapor (21). Under some conditions (for small concentrations of air in the mixture), the parameter of nonlinearity \( B/A \) is negative, but the coefficient

![Fig. 2. The small-signal sound velocity \( c \) (a) and the parameter of nonlinearity \( B/A \) (b) of the ternary mixture consisting of water, its vapor and dry air with separate volumes occupied by air and vapor. The mass concentration of the vapor \( x_2 \) has the values 0.01, 0.1, 0.3, 0.5, 0.9 from the lowest to the upper curve in every set. The horizontal axis presents the mass concentration of air \( x_3 \).]
of nonlinearity $\varepsilon = B/2A + 1$ remains positive over all the domain of the existing mixture, like in the binary mixture. Nonlinearity and sound velocity become smaller at small mass concentrations of vapor $x_2$.

Curves of the Fig. 3 present the parameter of nonlinearity $B/A$ of the mixture with mutual volume occupied by gases under different pressures, they correspond to the relative domain of ternary mixture existence (18).

![Fig. 3. Parameter of nonlinearity $B/A$ of the ternary mixture consisting of water, its vapor and dry air with mutual volume occupied by air and vapor; $p$ is the pressure of the mixture as a whole, $p_2 = 1$ atm is the partial pressure of vapor of water, and $x_2$ denotes the mass concentration of vapor in the mixture.](image)

### 5. Conclusions

Specific thermodynamic features of the ternary mixture consisting of air and water being in the phase equilibrium with its vapor result in interesting features of sound propagation. In both types of the mixture, with mutual and separate volumes occupied by gases, the sound velocity is considerably smaller than that in the pure water. The reason of it is that the basic part of a ternary mixture of any kind is the binary mixture consisting of liquid and its vapor being in phase equilibrium. A small-signal sound velocity in
the binary mixture is well studied [4, 5]. Figure 1 of the present study illustrates that the maximum sound velocity which may be achieved in the binary mixture consisting of water and its vapor at temperature $T = 373.15$ K and pressure $p_2 = 1$ atm, is about 450 m/s, while in pure water it equals approximately 1500 m/s. Figure 2 reveals that the addition of air increases somewhat the sound speed. The slow-down of the sound speed caused by phase transfer plays a less important role when a larger amount of air is present in the mixture.

The parameter of nonlinearity may have negative values, especially for small concentrations of air in the mixture, although the coefficient of nonlinearity $\varepsilon = B/2A + 1$ is positive. This also follows from the nonlinear features of the binary mixture possessing negative values of $B/A$, as follows from the calculations by the author and ARUTUNIAN, (Fig. 1b). The quantity $\varepsilon$ is a basic measure of finite-amplitude effects associated with the propagation of the progressive sound wave. It is positive for pure fluids except under extraordinary conditions, such as the neighborhood of a critical point, see [1].

It would be mistakably to find an analogue with ideal gases, where negative a value of $B/A$ results in the physically incorrect relationship $C_p < C_V$ because the specific thermodynamics of the binary mixture as a whole differs drastically from that of ideal gases, and the simple relation $B/A = C_p/C_V - 1$ is not true any more. It is not true even for pure water, for which $C_p \approx C_V$ under normal conditions, but $B/A \approx 6$. It is known that the parameter of nonlinearity is negative for some solids, such as fused quartz and Pyrex glass [1]. The growth of $B/A$ with increase of the mass concentration of air $x_3$ may be explained by “smoothing” of the binary mixture thermodynamics at phase equilibrium by adding a neutral gas. That makes the mixture closer to this one consisting of immiscible compounds. Figure 3 reveals the complex dependence of $B/A$ on pressure and mass concentration of vapor $x_2$. When $p$ tends towards $p_2 = 1$ atm, $p_3 \to 0$, and one goes to the limit of a pure binary mixture (the bold curve from the Fig. 1b). For high enough pressures of ternary mixture with mutual volumes occupied by vapor and gas, $B/A$ increases for small values $x_2$. It may be supposed that the increase in partial pressure of air with the decrease of $x_2$ makes the diffusion of vapor molecules to the surface of water and a further condensation more difficult. Therefore, the reason for “smoothening” of nonlinear distortions disappears. On the other hand, it is possible, that other mechanisms become dominant at high pressures: for example, the equations of state of ideal gases should be revised and so on.

All the computations have been undertaken for water vapor under the pressure $p_2 = 1$ atm and at temperature $T = 373.15$ K [7, 8]. The question about specific nonlinear features under other equilibrium thermodynamic conditions is open and needs additional investigations.

The theoretical predictions of the small-signal sound velocity and the character of nonlinear distortions of sound may be useful in the research of mass concentrations of compounds in a ternary mixtures. Some ultrasonic studies of specific ternary liquid mixtures (ternary mixtures of N,N-dimethylformamide + dietylketone + 1-alkanols) have been employed adequately for the investigation of the nature of intermolecular interactions in pure liquids and their mixtures [10, 11].
References


