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PARAMETER OF NONLINEARITY B/A OF THREE-COMPONENT SYSTEMS WITH SEPARATE VOLUMES OF LIQUID, ITS VAPOR AND A NEUTRAL GAS

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An expression of the excess entropy of a three-component mixture with separate volumes of liquid, vapor and neutral gas in terms of its excess pressure and density is obtained with accuracy up to quadratic nonlinear terms. The formulae of a small-signal sound speed and parameter of nonlinearity B/A defined by this expression depend on equilibrium mass concentrations of vapor and neutral gas and the initial pressure of the mixture. The only limitation is that the vapor and the inertial gas are ideal gases. Calculations of the sound velocity and the parameter of nonlinearity are presented for a mixture consisting of water and water vapor being in phase equilibrium and air.

Key words: parameter of nonlinearity B/A, coefficient of nonlinearity, three-component mixture with separate volumes of gas and vapor.

Notations

p	$(p_0, p' = p - p_0)$ pressure (unperturbed quantity, an excess quantity),
ρ	$(\rho_0, \rho' = \rho - \rho_0)$ density (unperturbed quantity, an excess quantity),
s	$(s_0, s' = s - s_0)$ entropy (unperturbed quantity, an excess quantity),
x	$(x_0, x' = x - x_0)$ mass concentration of the water vapor in the binary mixture, (unperturbed quantity, an excess quantity),
index 1	refers to the water,
index 2	refers to the water vapor,
index $1, 2$	refers to the binary mixture consisting of the water and water vapor,
index 3	refers to the air.

Constants

$R = 8.314$ J $\cdot$ mol^{-1}K^{-1} – the universal gas constant,
$\mu_1 = \mu_2 = 18.015 \cdot 10^{-3}$ kg $\cdot$ mol^{-1} – molar mass of the water and water vapor,
$\mu_3 = 28.96 \cdot 10^{-3}$ kg $\cdot$ mol^{-1} – molar mass of the air.

Equilibrium quantities

List of data relating to the equilibrium state $p = 101325$ Pa, $T = 373.15^\circ$K ([9, 11–13]):

ΔH = 40657 J $\cdot$ mol^{-1}, an enthalpy of vaporization of the water,

$\frac{d\Delta H}{dT} = -46.4$ J $\cdot$ mol$^{-1}\cdot$ K^{-1}, temperature gradient of ΔH,

$\gamma_1 = 5 \cdot 10^{-10}$ Pa^{-1}, compressibility under constant temperature of the water,

$\beta_1 = 8 \cdot 10^{-4}$K^{-1}, compressibility under constant pressure of the water,

ρ_1 = 958 kg $\cdot$ m^{-3}, unperturbed density of the water,

$\rho_2 = 0.588$ kg $\cdot$ m^{-3} unperturbed density of the water vapor,

$\rho_3 = 0.946$ kg $\cdot$ m^{-3}, unperturbed density of the air,

$\left(\frac{B}{A}\right)_1$ = 6.1, parameter of nonlinearity of the water,

$\left(\frac{B}{A}\right)_2$ = 0.33, parameter of nonlinearity of the water vapor,

$\left(\frac{B}{A}\right)_3$ = 0.4, parameter of nonlinearity of the air,

$C_{p,1}$ = 75.95 J $\cdot$ mol$^{-1}\cdot$ K^{-1}, heat capacity under constant pressure of the water,

$C_{p,2}$ = 33.26 J $\cdot$ mol$^{-1}\cdot$ K^{-1}, heat capacity under constant pressure of the water vapor,

$C_{p,3}$ = 29.10 J $\cdot$ mol$^{-1}\cdot$ K^{-1}, heat capacity under constant pressure of the air,

$C_v = C_p - \frac{T\beta^2\mu}{\gamma\rho}$, heat capacity under constant volume expressed through a heat capacity under constant pressure,

c_1 = 1543.4 m/s, a small-signal sound velocity in the water,

c_2 = 479.18 m/s, a small-signal sound velocity in the water vapor,

c_3 = 387.27 m/s, a small-signal sound velocity in the air.

1. Introduction

Any chemical interaction or phase transition between compounds of a multi-component mixture complicates essentially the mathematical model of wave propagation in such media and thereby the calculations of sound velocity and parameter of nonlinearity $\left(c^2 = \left(\frac{\partial p}{\partial \rho}\right)\Big|_{s=\text{const}},\ B/A = \frac{\rho}{c^2}\left(\frac{\partial^2 p}{\partial \rho^2}\right)\Big|_{s=\text{const}}\right)$.

The most simple mixture is that the consisting of immiscible fluids under the same pressure without chemical reactions and phase transitions. The calculations are based on the relations of superposition of specific volumes and changes in entropy per unit mass of every compound [1]. Final expressions for the sound speed and parameter of nonlinearity tend to those in a pure phase when mass concentrations of all other compounds tend to zero.

More complex mixtures are binary mixtures of liquid and vapor being in a phase equilibrium, and ternary mixtures where the vapor and neutral gas occupy a mutual volume. Mass transfer between phases essentially complicates calculations of the velocity and nonlinear parameters of sound. In contrast to multi-component systems of immiscible fluids, neither the velocity of sound nor the parameter of nonlinearity in binary mixtures in phase equilibrium go to a limit of those values in pure phases when the corresponding mass concentration tends to zero.

Basic results on thermodynamic features of binary mixtures were reported. There are classic results on calculation of sound velocity in the mixture consisting of water and water vapor [2], shock waves transforming the mixture into a one-phase substance [3], and the equation of state suitable for a large area of pressure [4] and so on. Ternary mixtures formed by involving a neutral gas into a binary mixture were studied recently by ARUTUNIAN [5]. It was shown that complete condensation of vapor never occurs in these systems. The results of Arutunian (areas of existing, small-signal sound speed) are essentially based on the limitations listed below:

1) the liquid is incompressible;
2) heat capacity under constant volume of liquid is constant;
3) heat of vaporization is constant;
4) density of the liquid is considerably larger than that of vapor;
5) the vapor is an ideal gas.

A special kind of multi-component systems are systems with separate volumes of vapor and neutral gas. The conditions of existing of such structures were investigated by ARUTUNIAN [3, 6]. They may be artificially created but are also popular as a result of human's activity. Molecules of vapor and gas do not mix when an impenetrable boundary appearing between them of the particles of the liquid became moistened by a some non-fleeting liquid ($H_{22}C_{10}O_4$ fits for water). Even in the absence of an impenetrable boundary, such systems may exist in some special cases: when intense heating makes the velocity of evaporation much larger than the velocity of diffusion of vapor molecules into gas and *vice versa*.

Systems with separate volumes of gas and vapor were investigated by Arutunian under five basic limitations listed before. These limitations simplify the calculations but may yield in a noticeable mistake when evaluations that need a correct account of higher order derivatives of thermodynamic values are proceeded. The first condition is incompatible with sound propagation in water. Obviously, this limitation is due to the fact that at the normal conditions sound velocity in a liquid is much larger than that in a gas. Any calculations of sound velocity or the parameter of nonlinearity essentially need the compressibility of the liquid. The latter does not agree with experimental data and may lead to an error in the parameter of nonlinearity of the fluid B/A which includes not only the heat capacity in the equilibrium state, but also its derivatives. The third condition does not allow to write the terms forming B/A in a correct manner but probably does not play a great role for a majority of mixtures. The forth limitation is quite reasonable when equilibrium values of density are considered but should be revised when higher order terms forming B/A are calculated. A precise evaluation of B/A needs at least the first four limitations to be revised.

The author derived formulae of the sound velocity and parameter of nonlinearity B/A using the fifth limitation only. The fifth limitation is not a principle point; all final formulae may be easily corrected in the view of a vapor obeying the equation of state for real gases [7]. A comparison these results with analogous ones by other authors shows high sensibility of the parameter of nonlinearity to the accuracy of calculations, in contrast to the sound velocity. So, calculations of the parameter of nonlinearity of a three-component mixture based on the roughly approximate formulae for a binary mixture (liquid and its vapor in phase equilibrium) could not give in principle a correct value of the parameter of nonlinearity.

The author is basing on the formula for sound velocity and the parameter of nonlinearity for a binary mixture to get the excess entropy of a mixture with separate volumes of gas and vapor as a whole in the terms of mixture: pressure and density.

2. Governing equations, sound velocity and parameter of nonlinearity of a binary mixture

Let us consider a binary mixture consisting of a liquid and its vapor in phase equilibrium. Density of the mixture $\rho_{1,2}$ is related to the densities of the liquid and vapor ρ_1, ρ_2 as follows (x marks mass concentration of vapor):

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

The vapor is an ideal gas in accordance to the fifth condition from the introduction and obeys a relation:

$$\rho_2 = \frac{p_2\mu_2}{RT}. \tag{2}$$

Index 1 marks values of the liquid, index 2 marks values of the vapor, and values with index $1,2$ relate to 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 phases and satisfies the equation of Clapeyron [2, 8]:

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

where the difference of their molar entropies is related to the change in enthalpy of vaporization of the liquid in the following way:

$$\Delta s = s_2 - s_1 = \frac{\Delta H}{T}\,. \tag{4}$$

Value ΔH is the enthalpy (heat) of vaporization slowly depending on temperature.

Equations (1)–(4) with both the following relations for partial and summary changes in entropy (5), form an initial point for further calculations.

$$
\begin{aligned}
s_1' &= \frac{\gamma_1 C_{v,1}}{T\beta_1}\left(p_2' - c_1^2\rho_1' - \left(\frac{B}{2A}\right)_1 \frac{c_1^2}{\rho_1}\rho_1'^2\right), \\
s_2' &= \frac{C_{v,2}}{p_2}\left(p_2' - c_2^2\rho_2' - \left(\frac{B}{2A}\right)_2 \frac{c_2^2}{\rho_2}\rho_2'^2\right), \\
s_{1,2}' &= (1-x)s_1' + xs_2' + x'\Delta s,
\end{aligned}
\tag{5}
$$

where $p_2' = p_2 - p_{2,0}$ is the excess pressure, $\rho' = \rho - \rho_0$, $s' = s - s_0$, $x' = x - x_0$ are excess density, change in entropy and mass concentration, C_v means heat capacity under constant volume. The same notations are used throughout the text, the index 0 for unperturbed values is omitted in the final expressions. Compressibilities under constant temperature and pressure, γ and β, respectively:

$$
\gamma = \frac{1}{\rho}\left(\frac{\partial\rho}{\partial p}\right)\bigg|_{T=\text{const}}, \qquad \beta = -\frac{1}{\rho}\left(\frac{\partial\rho}{\partial T}\right)\bigg|_{p=\text{const}}
\tag{6}
$$

are related to equilibrium state (p_2, T), and c_1, c_2 are velocities of sound in the pure phases:

$$
c_1^2 = \frac{C_{p,1}}{C_{v,1}\gamma_1\rho_1}, \qquad c_2^2 = \frac{C_{p,2}}{C_{v,2}}\frac{p_2}{\rho_2}.
\tag{7}
$$

The value x' may be thought as a nonlinear function of ρ_1', ρ_2' determined by Eq. (1). From the other side, the values ρ_1', ρ_2' may be expressed by p_2 at phase equilibrium as follows:

$$
\rho_1' = K_1 p_2' + Q_1 p_2'^2, \qquad \rho_2' = K_2 p_2' + Q_2 p_2'^2,
\tag{8}
$$

with values of K_1, K_2, Q_1, Q_2 determined by the following formulae:

$$
\begin{aligned}
K_1 &= \gamma_1\rho_1 - \frac{\beta_1\rho_1}{\dfrac{dp_2}{dT}}, \qquad K_2 = \frac{\mu_2}{RT} - \frac{\mu_2 p_2}{RT^2}\frac{1}{\dfrac{dp_2}{dT}}, \\
Q_1 &= 0.5\frac{\beta_1\rho_1\dfrac{d^2p_2}{dT^2}}{\left(\dfrac{dp_2}{dT}\right)^3} + 0.5\frac{\partial}{\partial p_2}(\gamma_1\rho_1) - 0.5\frac{\partial}{\partial T}(\beta_1\rho_1)\frac{1}{\left(\dfrac{dp_2}{dT}\right)^2} \\
&\quad + \frac{\partial}{\partial T}(\gamma_1\rho_1)\frac{1}{\dfrac{dp_2}{dT}}, \\
Q_2 &= 0.5\frac{\mu_2 p_2}{RT^2}\frac{\dfrac{d^2p_2}{dT^2}}{\left(\dfrac{dp_2}{dT}\right)^3} + \frac{\mu_2 p_2}{RT^3}\frac{1}{\left(\dfrac{dp_2}{dT}\right)^2} - \frac{\mu_2}{RT^2}\frac{1}{\dfrac{dp_2}{dT}}.
\end{aligned}
\tag{9}
$$

In the formula above, dp_2/dT is ((2)–(4) and $\rho_2 \ll \rho_1$ accounted):

$$\frac{dp_2}{dT} = \frac{p_2 \Delta H}{RT^2}. \tag{10}$$

Assuming in the quadratic terms that $p_2' \approx c_{1,2}^2 \rho_{1,2}'$ and taking into account Eqs. (8)–(10), one gets the expression for x' through mixture perturbations p_2', $\rho_{1,2}'$ as a quadratic function:

$$\begin{aligned} x' &= \left(\frac{(1-x)K_1\rho_2}{\rho_1^2} + \frac{xK_2}{\rho_2}\right) p_2' + \left(\frac{(1-x)Q_1\rho_2}{\rho_1^2} + \frac{xQ_2}{\rho_2}\right) p_2'^2 \\ &\qquad - \frac{\rho_2 \rho_{1,2}'}{\rho_{1,2}^2} + G \cdot p_2'^2, \\ G &= -\frac{K_2}{c_{1,2}^2 \rho_{1,2}^2} + \frac{\rho_2}{c_{1,2}^4 \rho_{1,2}^3} + K_1^2 \left(\frac{\rho_2^2}{\rho_{1,2}\rho_1^3} - \frac{\rho_2}{\rho_1^3}\right) \\ &\qquad + K_1 \left(\frac{K_2}{\rho_1^2} - \frac{2K_2\rho_2}{\rho_{1,2}\rho_1^2} + \frac{\rho_2^2}{c_{1,2}^2 \rho_{1,2}^2 \rho_1^2}\right). \end{aligned} \tag{11}$$

The change in the molar entropy of the mixture, accounting nonlinear quadratic terms, has therefore the form:

$$s_{1,2}' = \frac{\Delta H \mu_2 p_2}{RT^2 \rho_{1,2}^2 c_{1,2}^2} \left(p_2' - c_{1,2}^2 \rho_{1,2}'\right) - M p_2'^2, \tag{12}$$

where M is as follows:

$$\begin{aligned} M &= (1-x)\frac{\gamma_1 C_{v,1}}{T\beta_1} \left(\frac{B}{2A}\right)_1 \frac{c_1^2}{\rho_1} K_1^2 + x \frac{C_{v,2}}{p_2} \left(\frac{B}{2A}\right)_2 \frac{c_2^2}{\rho_2} K_2^2 \\ &\quad - \frac{\Delta H}{T} \left(\frac{(1-x)Q_1\rho_2}{\rho_1^2} + \frac{xQ_2}{\rho_2} + G\right) \\ &\quad + \left(\frac{\Delta H}{T^2} - \frac{1}{T}\frac{d(\Delta H)}{dT}\right) \left(\frac{(1-x)K_1\rho_2}{\rho_1^2} + \frac{xK_2}{\rho_2} - \frac{\rho_2}{\rho_{1,2}^2 c_{1,2}^2}\right) \frac{1}{\frac{dp_2}{dT}}, \end{aligned} \tag{13}$$

$c_{1,2}$ is the velocity of an infinitely small perturbation of the binary system

$$c_{1,2}^2 = \frac{\Delta H \mu_2 p_2 / (RT^2 \rho_2^2)}{x\left(-\frac{2R}{p_2} + \frac{\Delta H}{p_2 T_0} + \frac{C_{p,2} RT}{\Delta H p_2}\right) + (1-x)\left(-\frac{2\beta_1 \mu_2}{\rho_1} + \frac{\gamma_1 \Delta H p_2 \mu_2}{RT^2 \rho_1^2} + \frac{C_{p,1} RT}{\Delta H p_2}\right)}. \tag{14}$$

An analogous formula of LANDAU [2] relates to a mixture of incompressible water and does not include the term $-\frac{2\beta_1\mu_2}{\rho_1} + \frac{\gamma_1 \Delta H p_2 \mu_2}{RT^2 \rho_1^2}$, which is not of great importance except probably the mixtures with extremely small values of the gas fraction. Finally, $s'_{1,2} = 0$ results in a parameter $(B/A)_{1,2}$ for a binary mixture:

$$\left(\frac{B}{A}\right)_{1,2} = \frac{2MRT^2\rho_{1,2}^3 c_{1,2}^4}{\Delta H \mu_2 p_2}\,. \tag{15}$$

It is worthwhile noting that while calculating the nonlinear parameter, all the second-order terms of values that includes excess entropy, should be carefully accounted as well as the derivatives $d(\Delta H)/dT$. Moreover, the values of Q_1, Q_2, defined by (8), involve a second derivative d^2p_2/dT^2. The formula (15) is general and accounts the compressibility of the liquid phase that is not so important when the velocity of sound in mixture is calculated, but does play a role in the calculations of nonlinear parameters.

For a concrete binary mixture consisting of water and water vapor, the three last terms of Q_1 may be omitted in calculations due to small values of γ_1, β_1 and their derivatives in the vicinity of $p_2 = 101325$ Pa, $T = 373.15°$K[9]. Some data on the temperature behavior of β_1 in the vicinity of 100°C may be found in the paper of BATCHELOR [10], and on both coefficients, in the book edited by GRIGORIEV, MEILIKHOV [11].

The value $\left(\dfrac{\partial^2 V}{\partial p_2^2}\right)_{s=\mathrm{const}}$ (where $V = 1/\rho_{1,2}$) under conditions (1)–(5) of the introduction, was calculated by ARUTUNIAN [3]. It can be easily shown that this value relates to B/A in the following way:

$$\left(\frac{B}{A}\right)_{1,2} = c_{1,2}^4\rho_{1,2}^3\frac{\partial^2 V}{\partial p_2^2} - 2. \tag{16}$$

The value of B/A by the formula (15) is approximately -2 when $x \to 0$ and is very close to this of Arutunian (calculated by the author by use of Eq. (16) with the relative quantity of $\partial^2 V/\partial p_2^2$), while the corresponding values at $x \to 1$ differ greatly (0.5 and -0.5). So, the limitations of the formula by Arutunian results in essentially different values in the vicinity of the pure gas phase. Calculations were undertaken for the following equilibrium pressure and temperature of a binary mixture: $p = 101325$ Pa, $T = 373.15°$K.

3. A small-signal sound velocity and parameter of nonlinearity of a mixture with separate volumes of the vapor and neutral gas

The density of a mixture as a whole is:

$$\frac{1}{\rho} = \frac{1-x_3}{\rho_{1,2}} + \frac{x_3}{\rho_3} = \frac{1-x_2-x_3}{\rho_1} + \frac{x_2}{\rho_2} + \frac{x_3}{\rho_3}\,, \tag{17}$$

where x_3 is the constant mass concentration of the neutral gas. The mass concentration of the vapor in the binary mixture x relates to the mass concentration vapor in the hole mixture as follows $x_2 = x(1-x_3)$ $(x_2 \leq (1-x_3))$.

The very strong relations between all the compounds are given by equality of temperature and pressure over the mixture as a whole:

$$p_1 = p_2 = p_3 = p, \qquad T_1 = T_2 = T_3 = T. \tag{18}$$

It immediately gives a link between densities of both the gases (they are both ideal):

$$\rho_2/\mu_2 = \rho_3/\mu_3, \tag{19}$$

and, therefore, the next one (accounting Eq. (8)):

$$\rho_3' = \frac{\mu_3}{\mu_2}\left(K_2 p' + Q_2 p'^2\right). \tag{20}$$

Taking into account Eq. (17), the excess pressure of the binary mixture is:

$$\begin{aligned}\rho_{1,2}' = {} & \frac{\mu_3\rho_{1,2}^2 x_3\left(\mu_2 Q_2 \rho_3^2(x_3-1) + K_2^2\mu_3(\rho_3+\rho_{1,2}x_3-\rho_3 x_3)\right)}{\mu_2^2\rho_3^4(1-x_3)^2}p'^2 \\ & -\frac{x_3\left(\rho_3(x_3-1)-\rho_{1,2}x_3\right)^3}{\rho_3^4(1-x_3)^2}\rho'^2 - \frac{2K_2\mu_3\rho_{1,2}x_3\left(\rho_3+\rho_{1,2}x_3-\rho_3x_3\right)^2}{\mu_2\rho_3^4(1-x_3)^2}p'\rho' \\ & -\frac{\left(\rho_3(x_3-1)-\rho_{1,2}x_3\right)^2}{\rho_3^2(x_3-1)}\rho' + \frac{K_2\mu_3\rho_{1,2}^2x_3}{\mu_2\rho_3^2(x_3-1)}p'.\end{aligned} \tag{21}$$

The excess entropy of the unit mass of the ternary mixture is additive:

$$S' = x_3 s_3'/\mu_3 + (1-x_3)s_{1,2}'/\mu_1, \tag{22}$$

where s' marks the change in molar entropy.

The excess molar entropy of the neutral gas s_3' is as follows:

$$s_3' = \frac{C_{v,3}}{p}\left(p' - c_3^2\rho_3' - \left(\frac{B}{2A}\right)_3 \frac{c_3^2}{\rho_3}{\rho'}_3^2\right), \tag{23}$$

and the excess molar entropy of the binary mixture is given by Eq. (12).

Therefore, the excess entropy of the unit mass of a three-component mixture is expressed by the excess pressure and density as follows:

$$S' = L\left(p' - c^2\rho' - \left(\frac{B}{2A}\right)\frac{c^2}{\rho}{\rho'}^2\right), \tag{24}$$

with the values L, c, B/A:

$$L = \frac{-\mu_2\mu_3p^2\rho_3^2(x_3-1)\Delta H + c_{1,2}^2\rho_{1,2}^2x_3(C_{v,3}(\mu_2-c_3^2K_2\mu_3)R\rho_3^2T^2+K_2\mu_3^2p^2\Delta H)}{c_{1,2}^2\mu_2\mu_3pR\rho_{1,2}^2\rho_3^2T^2},$$

$$\begin{aligned}\frac{B}{A} = &-\frac{2\rho_{1,2}x_3 + (B/A)_{1,2}Z_1}{\rho_3(x_3-1)(Z_3 - c_{1,2}^2\mu_3\rho_{1,2}^2x_3(C_{v,3}(\mu_2 - c_3^2K_2\mu_3)R\rho_3^2T^2 + K_2\mu_3^2p^2\Delta H))^2}\\
&-\frac{\rho_{1,2}^3(c_{1,2}^4\mu_3^2p^2x_3Z_1\Delta H(Z_2(x_3-1)+\mu_3p^2K_2^2\mu_3(2+(B/A)_{1,2})\rho_{1,2}x_3))\Delta H}{\rho_3(x_3-1)(Z_3 - c_{1,2}^2\mu_3\rho_{1,2}^2x_3(C_{v,3}(\mu_2 - c_3^2K_2\mu_3)R\rho_3^2T^2 + K_2\mu_3^2p^2\Delta H))^2}\\
&-\frac{2(2+(B/A)_{1,2})c_{1,2}^2K_2\mu_3^2p^2x_3Z_1\Delta H}{\rho_{1,2}(-Z_3 + c_{1,2}^2\rho_{1,2}^2x_3(C_{v,3}(\mu_2 - c_3^2K_2\mu_3)R\rho_3^2T^2 + K_2\mu_3^2p^2\Delta H))},\end{aligned} \qquad (25)$$

which are functions of $x_2 = x(1 - x_3)$, x_3, p and other parameters of the initial state: temperature, heat of vaporization and so on, and Z_1, Z_2, Z_3 are expressed as follows:

$$\begin{aligned}Z_1 &= \rho_3 + \rho_{1,2}x_3 - \rho_3x_3,\\
Z_2 &= -(B/A)_3c_3^2C_{v,3}K_2^2\mu_3R\rho_3^3T^2 - 2c_3^2C_{v,3}\mu_2Q_2R\rho_3^4T^2\\
&\qquad + 2\mu_3p^2(\mu_2Q_2\rho_3^2 - K_2^2\mu_3\rho_3),\\
Z_3 &= \mu_2\mu_3p^2\rho_3^2(x_3 - 1)\Delta H.\end{aligned} \qquad (26)$$

Note that the formulae depend on x by means of $\rho_{1,2}$ according to Eq. (1). The values of $c_{1,2}$, $(B/A)_{1,2}$ are determined by the above formulae (14),(15).

The small-signal sound velocities predicted by Arutunian and Perelomova are very close to one another (Fig. 1). The difference becomes noticeable for large quantities of mass concentration of the air x_3 and does not exceed 5 percent. In Fig. 1a, curves corresponding to the ternary mixture are the dashed ones. It is taken into account that $x_2 \leq (1 - x_3)$. In the ternary mixture, vapor and neutral gas have a mutual volume. Accordingly to Arutiunian, the sound velocity in the ternary mixture is always somewhat smaller than that in the three-component mixture with separated volumes of the gas, vapor and liquid. Detailed calculations by the author reveal areas of smaller and larger values.

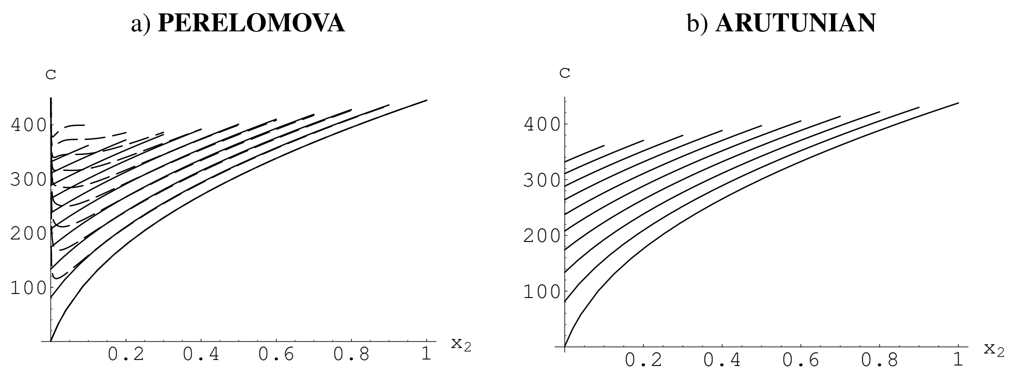

Fig. 1. Small-signal sound speed (m/s) calculated by formula (25) (a) and by the formula of Arutunian (b). The mass concentration of the air x_3 changes from 0 to 0.9 from the lower curve to the upper one. $p = 101325$ Pa, $T = 373.15°$K. In Fig. 1a dashed curves mark the velocity of the ternary mixture with partial pressure of the air $p_3 = 101325$ Pa related to the same temperature.

In spite of the close values of the small-signal sound speed in both sets of calculations (Perelomova and Arutunian, Fig. 1), the values of B/A are quite different (Fig. 2). There is no explicit formula for B/A in the paper of Arutunian, but the value of $\left(\dfrac{\partial V}{\partial p}\right)_{s=\mathrm{const}}$, $V = 1/\rho$. The author calculated a corresponding parameter of nonlinearity using c given by Arutunian and the following relation:

$$\frac{B}{A} = c^4 \rho^3 \frac{\partial^2 V}{\partial p^2} - 2. \tag{27}$$

It has been already stressed in the text, that the parameter of nonlinearity is highly sensible to the curvature of the sound velocity. Taking into account the compressibility of the liquid and going outside other limitations listed in the introduction, yield in different values of the parameter of nonlinearity. The larger concentration of the air x_3, the larger is the difference.

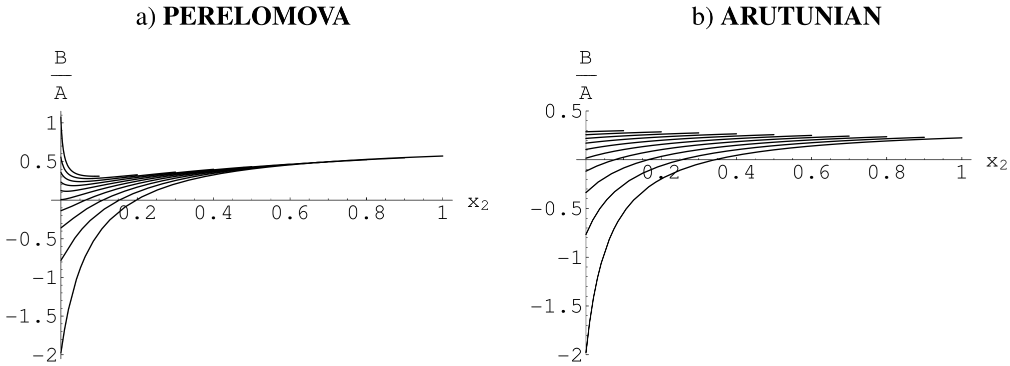

Fig. 2. Parameter of nonlinearity B/A calculated by formula (25) (a) and by the use of the expression of $\left(\dfrac{\partial V}{\partial p}\right)_{s=\mathrm{const}}$ of Arutunian (b). The mass concentration of the air x_3 changes from 0 to 0.9 from the lower curve to the upper one. $p = 101325$ Pa, $T = 373.15°$K.

4. Conclusions

The formulae derived by the author for the excess entropy of unit mass, the sound velocity and the parameter of nonlinearity of the mixture consisting of separate volumes of the gas, liquid and its vapor (24), (25) are general and apply to any such mixture under conditions discussed in the introduction. Among other advantages in comparison to previous results, the compressibility of a liquid being in phase equilibrium with its vapor is accounted. This is important, while the calculation of the parameter of nonlinearity B/A and the higher order ones C/A, D/A, ... because they are strongly dependent on the curvature of the thermodynamic functions.

Examples of calculations relate to a mixture of water, water vapor and air. The equilibrium temperature of the mixture is $T = 373.15°$ K and its equilibrium pressure is

$p = 101325$ Pa. The corresponding figures reveal close values of the small-signal sound velocity by the formulae of the author and those of ARUTUNIAN [3] (they do not exceed 5 percent) for large quantities of mass concentration of air in the mixture x_3, and a considerable difference of the parameter of nonlinearity B/A. The difference depends on the mass concentration of the air x_3. Values calculated by the author are even about 3 times larger when x_3 is about 1. The initial points of the model of a mixture treated by Arutunian are the limitations listed in the introduction. The only limitation used by the author is that the neutral gas and vapor are ideal gases. Formulae (25) are suitable for other mixtures consisting of a liquid being in phase equilibrium with its vapor and a neutral gas with separate volumes of fractions. They depend on three parameters: the mass concentrations of the gas fractions in the mixture x_2, x_3 and the pressure of the mixture p.

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