Sound velocity and acoustic nonlinearity parameter for fluids. Thermodynamic premises.

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Abstract

New theoretical formulae of the sound velocity and the B/A nonlinearity parameter for some fluids are presented in the paper. Semi-ideal and van der Waals models of gas are considered and the parameters are compared to experiment data. The liquid water model for equation of state, given by Jeffery and Austin analytical equation, is considered also and modified on the basis of acoustic data.
NOTATIONS:

- \( x \): space coordinate [\( m \)];
- \( t \): time [\( s \)];
- \( \rho \): density [\( kg/m^3 \)];
- \( p \): pressure [\( N/m^2 \)];
- \( v \): velocity [\( m/s \)];
- \( \eta, \zeta \): viscosity parameters;
- \( \chi \): heat conductivity parameter;
- \( x^*, t^*, \rho^*, p^*, v^* \): dimensionless variables;
- \( T \): absolute temperature [\( K \)];
- \( u \): internal energy per unit mass [\( J/kg \)];
- \( \rho_0, p_0, v_0, e_0, T_0 \): unperturbed values;
- \( \dot{\rho}, \dot{p}, \dot{v}, \dot{e}, \dot{T} \): perturbations;
- \( \beta \): characteristic scale of disturbance;
- \( \alpha \): coefficient responsible for amplitude of acoustic wave;
- \( D_1..D_5 \): dimensionless coefficients in evolution equations;
- \( E_1..E_5 \): coefficients in caloric equation of state;
- \( c \): linear sound velocity [\( m/s \)];
- \( B/A, C/A \): acoustic parameters of nonlinearity;
- \( s \): entropy [\( J \cdot kg^{-1} \cdot K^{-1} \)];
- \( c_{v(p)} \): heat capacity under constant pressure (volume) [\( J \cdot kg^{-1} \cdot K^{-1} \)];
- \( R \): the universal gas constant [\( J \cdot mol^{-1} \cdot K^{-1} \)];
- \( R_i \): individual gas constant [\( J \cdot K^{-1} \cdot kg^{-1} \)];
- \( \mu \): molar mass [\( kg/mol \)];
- \( f_{osc} \): number of oscillation degrees of freedom of a gas molecule;
- \( \theta_i \): characteristic temperature of oscillation [\( K \)];
- \( \gamma \): adiabatic gas constant (\( c_p/c_v \));
- \( \lambda, \alpha_1, v_B, T_B \), \( a, b_0, b_1, b_2 \), \( A_0, \Psi_1, \Psi_2, \Psi_3 \): constants in Jeffery-Austin equation for water;
1 Introduction

The experimental researches of some physical properties of different fluids, such the sound velocity and the acoustic nonlinearity parameters, are well known and advanced today [1, 2, 3, 4]. The theoretical basis on these problems, still have a lot of aspects to be studied properly.

One of the most interesting thing is the connecting of statistical thermodynamics and acoustic studies for gas or liquid, in order to disclose the micro-properties of a nonlinear propagation medium in a direct link to the macroscopic one. For example, knowing the structure on the molecular level for a model medium and comparing its acoustic properties to real one, we could conclude about a molecular structure of the fluid. In order to obtain the information we do not have to solve the system of basic equations. Obviously, we need both thermic and caloric equations of state, taking into account the thermodynamical relations between them [5].

There are used two different representations of the equations of state in our paper: the Taylor series for thermodynamic variables in a vicinity of a mechanical equilibrium point [6, 7, 8] and some analytical formulas. We start from well-known ideal/semi-ideal and van der Waals gases, comparing and discussing the results of the sound velocity and $B/A$ evaluations in both approaches and experiment. Hereby we consider an analytical (thermic) equation of state for a liquid water accordingly to a formula given recently by Jeffery and Austin [8]. Application of this equation to find sound velocity $c$ and $B/A$ is realized taking into account the equation for free energy. We presents a general form of the formula for the sound velocity and the nonlinear parameter $B/A$, (compare with the popular formula [1]) with and without using the mentioned Taylor series. (The theme of higher order parameters of fluid is presented in [10], look also in [11].)

The other interesting question is using the sound velocity, and nonlinear parameters, to test some new equations of state. We mean that an experimental value of the sound velocity (and $B/A$, $C/A$...) can be compare with a theoretical one, so then we can except or accept, a new model of medium. More, we have a mechanism to make some corrections, first of all we mean the adjusting parameters choice whilst covering more vide field of applications.

The following section includes formulating the physical problem on the mathematical level, similar like in [7, 9], with using projecting technique. Widely, this theme was raised earlier in [9]. Next sections contain general approach to the fluids parameters and its adaptation to some individual theoretical models.

2 Formulating of mathematical problem

The considered physical problem is the fluid medium (gas or liquid) being under acting the acoustic wave. A basic system of the hydrodynamic laws of conservation of momentum, energy and mass in one-dimensional flow is given by known
equations:
\[
\frac{\partial v}{\partial t} + v \frac{\partial v}{\partial x} + \frac{1}{\rho} \frac{\partial p}{\partial x} - \left( \frac{4}{3} \eta + \zeta \right) \frac{\partial^2 v}{\partial x^2} = 0, \\
\rho \frac{\partial u}{\partial t} + \rho v \frac{\partial u}{\partial x} + p \frac{\partial v}{\partial x} - \left( \frac{4}{3} \eta + \zeta \right) \left( \frac{\partial v}{\partial x} \right)^2 - \chi \frac{\partial^2 T}{\partial x^2} = 0, \\
\frac{\partial \rho}{\partial t} + \frac{\partial \rho v}{\partial x} = 0,
\]
and their simplified forms for nonviscous and non-heat-conducting fluids:
\[
\frac{\partial v}{\partial t} + v \frac{\partial v}{\partial x} + \frac{1}{\rho} \frac{\partial p}{\partial x} = 0, \\
\rho \frac{\partial u}{\partial t} + \rho v \frac{\partial u}{\partial x} + p \frac{\partial v}{\partial x} = 0, \\
\frac{\partial \rho}{\partial t} + \frac{\partial \rho v}{\partial x} = 0.
\]
In order to complete the physical problem we use the caloric and the thermic equations of state. The general forms of these thermodynamic equations, obtained by the Taylor series of two variables \((p, \rho)\) are:
\[
\rho_0 \dot{u} = E_1 \dot{p} + \frac{E_2 p_0}{\rho_0} \dot{\rho} + \frac{E_3}{\rho_0^2} \rho^2 + \frac{E_4 p_0}{\rho_0^2} \rho^2 + \frac{E_5}{\rho_0} \rho \dot{\rho} + \ldots \\
\dot{T} = \frac{\partial_1}{\rho_0 c_v} \dot{p} + \frac{\partial_2 p_0}{\rho_0^2 c_v} \dot{\rho} + \ldots.
\]
Obviously, we assume the quantities \(u, T, \rho, \rho, v\) have to be treated as \(z = z_0 + \dot{z}\) (index "zero" means an equilibrium value of \(z\) and "prime" means an addition, caused the sound wave), so the above formulae was written for the additions only. Finally, using dimensionless variables:
\[
v = \alpha c \varepsilon, \quad \dot{p} = \alpha c^2 \rho_0 \dot{\rho}_*, \quad \dot{\rho} = \alpha \rho_0 \dot{\rho}_*, \quad x = \beta x_*, \quad t = t_* \beta / c,
\]
where \(c\) is the linear sound velocity, given by
\[
c = \sqrt{\frac{\rho_0 (1 - E_2)}{\rho_0 E_1}},
\]
\(\beta\) means the characteristic scale of disturbance along \(x\) and \(\alpha\) is the coefficient responsible to the amplitude of the acoustic wave, we can formulate problem as the one matrix equation:
\[
\frac{\partial}{\partial t} \Psi + L \Psi = \ddot{\Psi} + \dddot{\Psi} + O(\alpha^3), \quad \Psi = \left( \begin{array}{c} v \\ \dot{p} \\ \dot{\rho} \end{array} \right).
\]
This is the nonlinear operator equation of time evolution, where:

\[
L = \begin{pmatrix}
0 & \frac{\partial}{\partial x} & 0 \\
\frac{\partial}{\partial x} & 0 & 0 \\
\frac{\partial}{\partial x} & 0 & 0
\end{pmatrix}
\]

\[
\tilde{\Psi} = \alpha \begin{pmatrix}
-v \frac{\partial v}{\partial x} + \rho \frac{\partial \rho}{\partial x} \\
-v \frac{\partial \rho}{\partial x} + \frac{\partial v}{\partial x} (\rho D_1 + \rho D_2) \\
-v \frac{\partial \rho}{\partial x} - \rho \frac{\partial v}{\partial x}
\end{pmatrix}
\]

(7)

The asterisks for the variables were omitted for simplicity, and \(D_1, D_2\) denote dimensionless coefficients, which are algebraic functions of \(E_1, E_2, E_3, E_4, E_5\) (see [9]):

\[
D_1 = \frac{1}{E_1} \left(-1 + 2 \frac{1-E_2}{E_1} E_3 + E_5\right),
\]

\[
D_2 = \frac{1}{1-E_2} \left(1 + E_2 + 2E_4 + \frac{1-E_2}{E_1} E_5\right).
\]

The second-order nonlinearity column \(\tilde{\Psi}\) will contribute to the \(B/A\) nonlinearity parameter. The constants \(A, B\) relate to coefficients \(D_j E_j\) in the following way:

\[
A = [(1-E_2)/E_1]p_0, \quad B = -(D_1 + D_2 + 1)((1-E_2)/E_1)p_0,
\]

\[
\frac{B}{A} = -D_1 - D_2 - 1.
\]

(8)

Now, let us return to the evolution equation (6). The new application of method of acting projectors was presented also in [6]. That is the simple way of separating the leftwards, rightwards and stationary modes of sound, which are responsible for the wave propagation effect in 'left' and 'right' directions, and for other effects (such as "streaming", see [4]). The separating of mode is done on the evolution equation level. Acting by one of mentioned projectors, i.e. unitary, orthogonal operators \(P_1, P_2,\) or \(P_3\)

\[
P_1 = \frac{1}{2} \begin{pmatrix}
1 & 1 & 0 \\
1 & 1 & 0 \\
1 & 1 & 0
\end{pmatrix}, \quad P_2 = \frac{1}{2} \begin{pmatrix}
1 & -1 & 0 \\
-1 & 1 & 0 \\
-1 & 1 & 0
\end{pmatrix}, \quad P_3 = \begin{pmatrix}
0 & 0 & 0 \\
0 & 0 & 0 \\
0 & -1 & 1
\end{pmatrix}
\]

on the evolution equation gives us a new form of wave equation:

\[
\frac{\partial}{\partial t} P_i \Psi + P_i L \Psi + P_i \tilde{\Psi} = 0, \quad i = 1, 2, 3,
\]

(9)

and introduces the sound velocity \(c\). The simplified version of the equation, neglecting heat conductivity and viscosity of medium, has form:

\[
\frac{\partial \rho_n}{\partial t} + c_n \frac{\partial \rho_n}{\partial x} + \sum_{i,m} \varepsilon \frac{\rho_n}{\partial x} \frac{\partial \rho_m}{\partial x} + \ldots = 0.
\]

(10)
\[ i = 1, 2, 3; \quad m = 1, 2, 3; \quad n = 1, 2, 3; \quad c_1 = 1; \quad c_2 = -1; \quad c_3 = 0; \]

where \( T \) denotes some coefficients matrix, and it is built with algebraic sums of \( D_1 \) and \( D_2 \), for \( n=1 \):

\[
\begin{vmatrix}
Y^1_{i,m} & m = 1 & m = 2 & m = 3 \\
\begin{array}{ccc}
i = 1 & & \\
-1 & -D_3 - D_2 + 1 & D_1 + D_2 - 1 & 0 \\
i = 2 & -D_3 - D_2 - 3 & D_1 + D_2 - 1 & 0 \\
i = 3 & -D_2 - 1 & D_2 - 1 & 0 \\
\end{array}
\end{vmatrix}
\]

We have to remember that the below form of equation is written for dimensionless variables.

### 3 Velocity of sound and B/A parameter in medium

In order to apply our considerations for some different models of fluids, not only ideal gas, we use the general expression for the sound velocity. Here, the sound velocity \( c \) takes the part of coefficient in the wave equation.

\[
c^2 = \left( \frac{\partial p}{\partial \rho \partial T} \right)_{S,p=p_0,T=0} (11)
\]

Index ‘S’ means obviously that entropy is constant, however in practice it is enough to assume the reversible adiabatic process \[4].

The sound velocity dependence on temperature is written well in the experimental acoustic papers. So, some experimental figures show linear dependence \( c \) on \( T \) for majoritity of liquids. However, it must be notice, that the sound velocity grows due temperature to 74ºC and next becomes smaller for liquid water case. These special forms of curves \( c(T) \)-dependence are known in literature as Willard curves. The peculiarities of water result from long-range order, strong polarity and strong association of water molecules.

The previous papers providing experimental data of \( B/A \) such \[1, 2, 3\] and later papers, show that the ratio \( B/A \) generally increases slowly with temperature, although there are some exceptions. The contribution to \( B/A \) from temperature changes is smaller than one due pressure changes.

#### 3.1 General formulae for nonlinearity parameters

To find a formula for the sound velocity we need two equations of state: \( p = p(\rho, T) \), \( U = U(\rho, T) \) and the first law of thermodynamics: \( dU = TdS - pdV \), where \( S \) means entropy, in form:

\[
du = Tds + \frac{p}{\rho^2}d\rho.
\]

(\( s, u \) are variables expressed per unit mass.) The differentials \( dp \) and \( du \) we take as:

\[
\begin{align*}
dp &= \left( \frac{\partial p}{\partial T} \right)_\rho dT + \left( \frac{\partial p}{\partial \rho} \right)_T d\rho = \beta_1 dT + \beta_2 d\rho
\end{align*}
\]
\[
du = \left( \frac{\partial u}{\partial T} \right)_\rho \, dT + \left( \frac{\partial u}{\partial \rho} \right)_T \, d\rho = \beta_3 dT + \beta_4 d\rho
\]

Comparing suitably the expressions and introducing them to the first law of thermodynamics equation, one can obtain a formula:

\[
\frac{dp}{d\rho} = \frac{\beta_1}{\beta_3} \left( \frac{p}{\rho^3} - \beta_4 + \frac{\beta_3 \beta_2}{\beta_1} \right) + \frac{\beta_1}{\beta_3} \frac{ds}{d\rho}, \tag{12}
\]

Next, we can do an assumption of adiabatic process of propagating sound, so finally:

\[
c^2 = \frac{\beta_1}{\beta_3} \frac{p}{\rho^3} - \frac{\beta_1 \beta_4}{\beta_3} + \beta_2. \tag{13}
\]

where

\[
\beta_1 = \left( \frac{\partial p}{\partial T} \right)_\rho, \quad \beta_2 = \left( \frac{\partial p}{\partial \rho} \right)_T
\]

\[
\beta_3 = \left( \frac{\partial u}{\partial T} \right)_\rho, \quad \beta_4 = \left( \frac{\partial u}{\partial \rho} \right)_T
\]

That is a new approach, without using of Taylor series for variables.

If we use the Taylor expansion for relation between pressure and density, and limit ourselves to quadratic terms, we will get the expression for \( B/A \) nonlinear parameter \(^1\) in form:

\[
\frac{B}{A} = \frac{\rho}{c_0^2} \left( \frac{\partial^2 p}{\partial \rho^2} \right)_{\rho_0, S} = \frac{\rho_0}{c_0^2} \left( \frac{\partial^2 c}{\partial \rho} \right)_{\rho_0, S}. \tag{14}
\]

### 3.2 Ideal and semi-ideal gas model

For ideal gas we receive the coefficients in forms: \( E_1 = E_4 = 1/(\gamma - 1), E_2 = E_5 = -1/(\gamma - 1), E_3 = 0, D_1 = -\gamma, D_2, \) so using the mentioned equation \(^5\) we receive \(^4\):

\[
c = \sqrt{\frac{\gamma \rho_0}{\rho_0}}
\]

where \( \gamma = C_p/C_V. \)

\[
B/A = \gamma - 1, \quad C/A = (\gamma - 1)(\gamma - 2)
\]

The semi-ideal gas model accepts energy of oscillation of molecule, and omits energy of rotation, because it is significant for very low temperatures and light gases only. The model concerns polyatomic gases only, because for monoatomic ones we have the same formulas as before.

\[
(Mc_v)_{sid} = (Mc_v)_{id} + (Mc)_{osc} + \Delta(Mc)_{rot}
\]

We use the Einstein – Planck formulae for vibrational specific heat:

\[
(Mc)_{osc} = (MR) \sum_{i=1}^{I_{osc}} \frac{\theta_i}{T}^2 \frac{e^{\theta_i/T}}{(e^{\theta_i/T} - 1)^2}
\]
by using which we get the equation for internal energy for semi–ideal gases [6]:

\[ u = u_{id} + \frac{MR}{\mu} \sum_{i} \frac{\theta_i}{e^{\theta_i/T} - 1} \tag{15} \]

where \( M_c, MR, \mu, f, \theta_i \) – vibrational specific heat, universal gas constant, molar mass, number of degrees of freedom of a molecule and characteristic temperature in correspond order. According to (5) the sound velocity formula looks finally:

\[ c^2 = R_i T \left(1 + \left(\frac{1}{\gamma - 1} + \sum_i \left(\frac{\theta_i}{T_0}\right)^2 e^{\theta_i/T_0} \left(e^{\theta_i/T_0} - 1\right)^{-2}\right)^{-1}\right) \tag{16} \]

A formula for \( B/A \) has a more cumbersome form:

\[
B/A = - \frac{E_2}{C_1} \left\{ -1 + \frac{1 + E_1}{C_1} \sum_i \left(C_{2i} C_{3i}\right) + C_0 \right\} + \frac{E_2}{E_1} \left\{ 1 + \frac{2}{\gamma - 1} + \sum_i \left(C_{4i} C_{5i}\right) + \frac{1 + E_1}{C_1} C_0 - E_1 \right\} \tag{17}
\]

where some new symbols mean accordingly:

\[
C_0 = -\frac{1}{\gamma - 1} + \sum_i \left(C_{2i} \left(C_{3i} - 1\right)\right)
\]

\[
C_1 = \frac{1}{\gamma - 1} + \sum_i C_{2i}
\]

\[
C_{2i} = \left(\frac{\theta_i}{T_0}\right)^2 \frac{\exp(\theta_i/T_0)}{\left(\exp(\theta_i/T_0) - 1\right)^2}
\]

\[
C_{3i} = -2 - (\theta_i/T_0) + 2(\theta_i/T_0) \frac{\exp(\theta_i/T_0)}{\left(\exp(\theta_i/T_0) - 1\right)}
\]

\[
C_{4i} = (\theta_i/T_0)^3 \frac{\exp(\theta_i/T_0)}{\left(\exp(\theta_i/T_0) - 1\right)^2}
\]

\[
C_{5i} = -1 + 2 \frac{\exp(\theta_i/T_0)}{\left(\exp(\theta_i/T_0) - 1\right)}
\]

The semi–ideal gas model has provided the quite correct data for polyatomic gases, like \( CO_2, CH_4, \) for any monoatomic (no oscillations) and diatomic gases we have not interesting difference for both models: semi–ideal and ideal one. Some results for a few gases are presented in Table 1 and the temperature dependence of \( c \) and \( B/A \) for \( CO_2 \) is shown at Fig.1. and Fig.2. (more in [9]).

| Gas   | Model of ideal gas | Model of semi–ideal gas | Experimental data |
|-------|--------------------|-------------------------|------------------|
| He    | 972.9              | 972.9                   | 971              |
| CO2   | 262.2              | 255.0                   | 256.7            |
| CH4   | 434.7              | 431.3                   | 430              |

**TABLE 1.** All values in the table are obtained for \( T = 273.15K. \)
**Figure 1.**

$CO_2$. Comparison of temperature dependence of sound velocity for both theoretical models in 200-480 K range of temperature.

**Figure 1a.**

$CO_2$ and $CH_4$. Differences of sound velocities $c_{sid} - c_{sid}$ for $N_2$, $CO$ and $CO_2$ gases.
3.3 Van der Waals gas model

Van der Waals gave the famous equation of state for gas model in 1873 year. That is convenient to use the mentioned equation in form:

\[
p = \frac{\rho R_i T}{(1 - b \rho)} - \dot{a} \rho^2 \quad \text{and} \quad e = c_v T - \dot{a} \rho, \quad (18)
\]

where \( R_i = R/\mu \) means individual constant for gas, \( \dot{a} = a/\mu^2, \dot{b} = b/\mu \) - van der Waals constants and \( R_i, e \) and \( c_v \) denote some values per unit mass. Calculating of the sound velocity \( c \), according to the (5) gives:

\[
c^2 = R_i^2 T \left( 1 - \left( \frac{2 c_v a (1 - b \rho)}{R_i} - c_v \frac{(p + a \rho^2) b}{R_i} - \frac{c_v (p + a \rho^2) (1 - b \rho)}{\rho^2 R_i} - a \right) \rho^2 p^{-1} \right) c_v^{-1} (1 - b \rho)^{-1}
\]

and by the new formula (13), gives a formula:

\[
c^2 = R_i T \left( \frac{\gamma - 1}{(1 - b \rho)} + 1 + \frac{\rho b}{(1 - b \rho)} \right)^{-1} - 2 \dot{a} \rho; \quad (20)
\]

Using (8) provides \( B/A \) in follow form:

\[
\frac{B}{A} = \left\{ R_i^2 p + 2 R_i c_v \dot{a} b \rho^3 + R_i c_v \dot{a} \rho + \dot{a} R_i^2 \rho^2 + 6 c_v^2 \dot{a} b \rho^3 + 2 c_v R_i \dot{b} \rho - 2 c_v^2 \dot{a} b \rho^4 + 2 c_v \dot{b} \rho^2 \right\} \left( (R_i p - c_v \dot{a} \rho^2 + 2 c_v \dot{a} b \rho^3 + c_v \dot{a} \rho + R_i \dot{a} \rho^2) c_v (1 - b \rho) \right)^{-1}
\]

(21)

Table 2. contains a comparison of some results for sound velocity for 273.15K. Fig.3. presents the theoretical curve of pressure dependence for \( c \).
### Table 2

| Gas     | Model of ideal gas | Laplace formula | Model of van der Waals gas | Experimental data |
|---------|--------------------|-----------------|-----------------------------|-------------------|
| He      | 970.9              | 971             | 970.7                       | 971               |
| H2      | 1259.9             | 1261            | 1259.2                      | 1286              |

All values in the table are obtained for $T = 273.15K$.

**Figure 3.**

$CO_2$. Comparison of theoretical (van der Waals model) and experimental values [12] of sound velocity for changing pressure. ($CO_2$, 323.95K, 0.3MHz)

The van der Waals equation of state in its standard form, give good results for some gases, but is not valid for many of liquids, in particular for water.

### 3.4 Liquid water model

**An analytical equation of state for liquid water**

The trials of “build” an analytical equation of state for liquid water were made. The one of the newest is the Song–Mason–Ihm equation [13] and its modifications, for the polar fluid, made by Jeffery and Austin [8]:

$$\frac{p}{\rho RT} = 1 - b_0 \rho - \frac{a \rho}{RT} + \frac{\alpha_1 \rho}{1 - \lambda b \rho}$$  \hspace{1cm} (22)

where $\rho$ is expressed in ($mol/m^3$) unit and function $b(T)$ has form:

$$b(T) = v_B \left(0.25e^{1/(2.3T/T_B+0.5)} - b_1 e^{2.3T/T_B} + b_2\right)$$

The constants used by authors of paper have the following values: $\lambda = 0.3159$; $\alpha_1 = 2.145v_B$; $b_0 = 1.0823v_B$; $b_1 = 0.02774$; $b_2 = 0.23578$; $v_B = 4.1782 \times 10^{-5}m^3/mol$; $T_B = 1408.4K$; $a = 0.5542 P \text{am}^9/mol^2$.

The equation of state for free energy proposed by Jeffery and Austin for $T > 4^\circ C$ has form:

$$F = A_1(\rho, T) - RT\Psi(T),$$

$$A_1 = RT\log\rho - RTb_0 \rho - a \rho - \frac{RT\alpha_1}{\lambda b(T)} \log(1 - \lambda b(T) \rho) - RT(-3\log\Lambda + 1) + A_0,$$
\[ \Psi = \Psi_1 + \Psi_2 \frac{T_B \lambda b(T)}{T_{\alpha_1}} + \Psi_3 \frac{T_B}{T}, \]

where: \( A_0 = 21.47 \text{kJ/mol}, \Psi_1 = 5.13, \Psi_2 = 20.04, \Psi_3 = 2.73 \), a \( \Lambda \) means temperature wavelength:

\[ \Lambda^2 = \frac{R^{5/3} h^2}{2 \pi m K_B^{8/3} T}. \]

In order to find the acoustic wave propagation velocity according to [13] in discussed medium, we make the following calculations for adiabatic process. The known expression for free energy will make possible finding internal energy per unit mass. In statistical physics: \( U = F - T \left( \frac{\partial F}{\partial T} \right)_V \), so \( dU = dF - dT F_T - TdF_T \). Here, bottom index means partial differential \( \frac{dF}{dT} \). We can write:

\[
\begin{align*}
\frac{dF}{dT} &= dA_1 - RdT \Psi - RT \Psi_T dT, \\
F_T &= A_{1T} - R\Psi - RT \Psi_T,
\end{align*}
\]

\[
\begin{align*}
\frac{dF_T}{dT} &= dA_{1T} - Rd\Psi - RdT \Psi_T - RT \Psi_{TT} dT, \\
dA_1 &= A_{1T} dT + A_{1\rho} d\rho
\end{align*}
\]

and in the same way like above we obtain the equation:

\[
d\rho \left( A_{1\rho} - T A_{1T\rho} + \frac{mp}{\rho^2} \right) + dT \left( -T A_{1TT} + 2RT \Psi_T + RT^2 \Psi_{TT} \right) = 0
\]

Sound velocity and B/A in liquid water

and finally:

\[ c^2 = \frac{\left( A_{1\rho} - T A_{1T\rho} + \frac{mp}{\rho^2} + \frac{\partial}{\partial T} TA_{1TT} - \frac{\partial^2}{\partial T^2} 2RT \Psi_T - \frac{\partial^2}{\partial T^2} RT^2 \Psi_{TT} \right) \beta_1}{TA_{1TT} - 2RT \Psi_T - RT^2 \Psi_{TT}}. \quad (24)\]

The expression of the nonlinear parameter B/A, received by using [14] has more complicated form, but it is not difficult to calculate some values using a computer.

Results for analytical model of liquid water

Authors tested Jeffery-Austin analytical equation of state for liquid water [8], being a development of [13]. Below we present some diagrams for the sound velocity and the nonlinear parameter B/A. The equation seems to be rather sensible for small changes of constants. Some results of \( c \) and \( B/A \) for the Jeffery-Austin equation differ from some experimental data (for 5 – 55°C temperatures), what was shown on the following figures (from Fig.4. to Fig.7.).
Figure 4.
Water. Dependence of sound velocity on temperature in $10^5$ Pa pressure.
Figure 5.
Water. Dependence of sound velocity on pressure, T = 303.15 K.

Figure 6.
Water. Dependence of $B/A$ parameter on temperature in $10^5$ Pa pressure.
However, the most interesting and worthy to underlining is fact we have a mechanism that makes possible testing and even correcting the equations of state. One of some various possible corrections is changing the constants: $\lambda = 0.244$ instead of $0.316$, $b_0 = -0.000026$ instead of $0.000045$ and $\psi_2 = 22.04$ instead $20.04$. The figures above shows compatibility that changed model to some experiments. The presented corrections have an example character only.

4 Conclusions

1. The new presented formula for the sound velocity is better than the earlier known one, used by the other authors, because of no necessary using of Taylor series, we have no need to limit ourselves to some first expressions in that expansion. Although, the values given by the both of these methods are the same in the semi-ideal and van der Waals gas model cases, probably we can expect interesting results of comparison for more complicated models of fluids. Undoubtedly, this is the small step forward in the theory.

2. Connecting thermodynamic physics and acoustics seems to be an interesting source of information about considered medium. We make a sensitive mechanism to test and correct theoretical models of various fluids, using of some
experimental data for $c$ and $B/A$. In future, incorporating the links between statistical physics and thermodynamics, it could be possible concluding about intermolecular potentials and molecular structure of medium from acoustic researches of fluids.

References

[1] R. Beyer, Parameter of Nonlinearity in Fluids, JASA, 32(6), 719-721, 1960.

[2] Coppens A., Beyer R. and others, Parameter of Nonlinearity in Fluids. II, JASA, 33(1), 797-804, 1965.

[3] Coppens A., Beyer R. and Ballou J., Parameter of Nonlinearity in Fluids. III. Values of Sound Velocity in Liquid Metals, JASA, 41(6), 1443-1448, 1967.

[4] S. Makarov, M. Ochmann, Nonlinear and Thermoviscous Phenomena in Acoustics, Part I, Acustica, Acta Acustica 82, 579-606, 1996.

[5] Lee J.F., Sears F.W., Turcotte D.L., Statistical thermodynamics, Addison–Wesley Publishing Company, London 1963.

[6] A.A. Perelomova, Projectors in Nonlinear Evolution Problem: Acoustic Solitons of Bubbly Liquid, Applied Mathematics Letters, 13, 2000.

[7] A.A. Perelomova, Directed Acoustic Beams Interacting with Heat Mode: Coupled Nonlinear Equations and the Modified KZK Equation, Acta Acustica, 87(1), 176-183, 2001.

[8] C. A. Jeffery, P.H. Austin, A new analytic equation of state for liquid water, J. Chem. Phys., Vol. 110, No. 1., 484-496, 1999.

[9] A. Perelomova, S.Leble, M.Kušmirek-Ochrymiuk, Nonlinear Evolution of the Acoustic Wave in a Semi-Ideal Gas, Archives of Acoustics, 26(4), 351-360, 2001.

[10] L. Bjorno and K. Black, U. Nigul and J. Engelbrecht (Eds.), Nonlinear Deformation Waves, Springer Verlag, pp.355-361, 1983.

[11] S. Leble, I. Vereshchagina, KZK equation with cubic terms and virial coefficients. Acta Acustica (85) 1999.

[12] A.N. Babichev, N.A. Babushkina, A.M. Bratkovski et al, Physical Values. Ergoatomizdat Moskva 1991 (in russian).

[13] G. Ihm, Y. Song, E. Mason, J. Chem. Phys., Vol. 94, 1991.